The Dow Chemical Company
Midland, Michigan 48674

Michigan Operations
May 1, 2006

VIA FEDERAL EXPRESS

Mr. George Bruchmann
Chief, Waste and Hazardous Materials Division
Michigan Department of Environmental Quality
Constitution Hall
525 W. Allegan Street
P.O. Box 30473
Lansing, MI 48909

Re: Dow Responses to the Michigan Department of Environmental Quality's (MDEQ) March 2 and April 13, 2006 Notices of Deficiency

Dear Mr. Bruchmann:

This letter and its enclosures respond to the comments in MDEQ's March 2 and April 13, 2006 Notices of Deficiency (NODs) regarding the Tittabawassee River and Midland Area Soils Remedial Investigation Work Plans (RIWPs) for which MDEQ sought a response by May 1, 2006. This May 1, 2006 date is in accordance with the letter dated April 10, 2006 from Mr. Sygo and your letter dated April 13, 2006. As set forth in those letters, a number of additional comments in both the March 2 and April 13 NODs are due for response by Dow on December 1, 2006.

As MDEQ is aware, Condition XI.B.5 of Dow's license provides Dow sixty days to respond to any NOD issued by MDEQ. Accordingly, Dow should have until June 12, 2006 to respond to MDEQ's April 13 NOD. At MDEQ's request and in the effort to move ahead, Dow has sought to respond as best it could in the limited time available since receipt of the April 13 NOD to the comments in that NOD for which MDEQ sought a response by May 1, 2006. Dow is responding to the items in the April 13 NOD for which a request was made to respond by May 1, even for those comments or requests that do not appear to be deficiencies in the original RIWPs. However, Dow reserves the right to supplement its response by June 12, 2006.

The current set of comments and responses focuses on the common goal of beginning data collection in the field this summer in order to gain a better understanding of site conditions and exposure potential, which, in turn, will serve as a solid foundation for later activities. To help ensure that field work can begin as soon as possible, Dow's responses include a number of work and study plans and other supporting documents for MDEQ's consideration. Enclosed please find **Response of Dow to MDEQ's Notices of Deficiency,** together with the following attachments:

Attachment A	**Sampling and Analysis Plan Development Overview – Tittabawassee River**
Attachment B	**Revised Tittabawassee River and Midland Area RIWP Schedules**
Attachment C	**Conceptual Human Exposure Models**
Attachment D	**PCOI Identification and Development of Target Analyte List**
Attachment E	**Activity Survey Study Plan**
Attachment F	**Site Specific Exposure Study Plans** 1. **Fish Tissue Study Plan** 2. **Game Tissue Study Plan** 3. **Domestic Livestock Study Plan** 4. **Garden Vegetable Study Plan** 5. **Stationary Airborne Agricultural Dust Study Plan** 6. **Personal Airborne Dust Exposure Study Plan**
Attachment G	**Comparison of Dioxin Analytical Results (Round Robin)**
Attachment H	**Soil/Dust/Sediment Exposure Data Quality Objectives**

The *Sampling Approach in Support of Bioavailability Study, Midland Soils* is being supplied under separate cover to MDEQ today.

We believe that the modifications to Dow's proposed investigatory approach, as described in the above enclosures and made in response to the comments of MDEQ and others, are consistent with the approved Scopes of Work (SOWs) and will, as a general matter, expedite and improve their implementation. The SOWs contain "preliminary" RI schedules that differ in some aspects from the updated and more detailed RI schedules submitted with this letter. (*See* SOWs, Figure 2). As with the SOW schedules, we have proposed these updated and, we believe, aggressive schedules in good faith; however, like the SOW timelines, these new RI schedules should be read as contingent based on assumed timeframes for science advisory panel reviews as well as agency review and approval. (*See* SOWs, Section IV).

Consistent with typical corrective action processes and the phased nature of remedial investigation planning once approved by MDEQ as part of the RIWPs, it is our understanding that the new schedules will be automatically incorporated into Dow's operating license and will take the place of the earlier-incorporated SOW schedules. (*See* Dow Operating License Part XI.B.4 and XI.B.5 ("Upon approval . . . the RI Work Plan becomes an enforceable condition of this license. The licensee shall implement the approved RI Work Plan in accordance with the schedule in the RI Work Plan.")). Therefore, separate and formal amendments to the SOWs -

proposed by Dow and approved by MDEQ - are not necessary. MDEQ's approval of the RIWPs (or parts thereof) and related schedules will convert the approved plans and schedules into enforceable conditions of the license. As such, the revised schedules will then serve to guide activities going forward in lieu of the preliminary schedules set forth in the SOWs.

Continued cooperation, discussion and hard work will undoubtedly be needed as work progresses and more information are developed. The RIWPs will require further modification as Dow and the MDEQ continue to work through MDEQ's comments and agree to modifications of the draft RIWPs. We appreciate the MDEQ's input to date, including its participation in recent field activities, and we look forward to working with MDEQ closely and regularly over the coming months. In this regard, we currently have the next meeting with MDEQ scheduled for May 11, 2006 and anticipate additional conference calls with MDEQ before that time.

We look forward to working with you and the MDEQ staff to meet the goal of commencing field work for the summer season.

Regards,

Ben Baker

Ben Baker
Senior Environmental Project Leader
Michigan Operations
47 Building
Midland, MI 48667

cc: Jack Bails, Public Sector Consultants
Greg Rudloff, US EPA
Frank Ruswick, Jr., MDEQ
Jim Sygo, MDEQ

Response to Notice of Deficiencies

This response should be read together with its cover letter dated May 1, 2006. The numbered items below correspond to the numbered comments in each Notice of Deficiency.

Response to March 2, 2006 Notice of Deficiency

1. General - Schedules

The schedules for the Tittabawassee River Remedial Investigation Work Plan (River RIWP) and the City of Midland Remedial Investigation Work Plan (Midland RIWP) have been revised to address MDEQ's comments and to reflect discussions with MDEQ since the River RIWP and Midland RIWP were originally submitted. The revised schedules are provided in Attachment B.

2. General – RI Strategy and Phasing

Since March 2, 2006, Dow and MDEQ have discussed on several occasions the rationales for the proposed approaches to Midland and Tittabawassee River and floodplain investigations. As discussed in more detail in the attached documents, the purpose of the proposed phasing of sampling and exposure studies in both areas is to ensure that the remedial investigation is both effective in terms of acquiring the information necessary to make risk-based remedial decisions and efficient in terms of the time and cost of collecting the necessary data. See the revised schedules in response to Comment 1 and the exposure study plans provided in response to Comment 16, below.

Tittabawassee River

An overall GeoMorph™-based remedial investigation strategy and proposed schedule was presented to MDEQ in meetings on March 14 and April 12, 2006. The GeoMorph™ Sampling and Analysis Plan (SAP) for the Tittabawassee River, to be submitted on June 1, 2006, will detail this strategy, and provide as much of a comprehensive and detailed schedule as can be predicted at this time. The GeoMorph™ detailed site characterization report, in combination with its companion human health risk assessment (HHRA) and ecological risk assessment (ERA) documents, will address the applicable and appropriate requirements of R 299.5528(3) for the Tittabawassee River. The GeoMorph™ characterization report is scheduled for submission in February 2007 for discussion and review before the 2007 field sampling season and the next round of activities. Further information about the GeoMorph™-based approach is provided below in response to Comments 5, 6, and 7.

Midland

The "*Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study*" (Support Study), which was originally submitted to MDEQ on

November 1, 2005, and revised and resubmitted on January 17, 2006, will be further revised and submitted on June 1, 2006. In addition to providing information necessary to support a bioavailability study, if one is conducted, this pre-RI study will aid the design of detailed sampling in Midland by providing information on the range of dioxin/furan concentrations and other Target Analytes (TAs) (if any) present in the Midland Study Area. The Support Study will also provide preliminary information on the spatial distribution of any TAs.

The detailed soil sampling design will follow the Support Study and be implemented following the development of alternative criteria under the terms of the Framework for an Agreement and this process will be outlined in the HHRA work plan. The detailed soil sampling design, in combination with the HHRA, will address the applicable and appropriate requirements of R 299.5528(3) for the Midland Study Area. See the revised schedules and the exposure study work plans provided in response to Comment 16, below.

Although R 299.5528(2) (a) does not require identification of potential remedial alternatives in remedial investigation work plans, Dow notes that all of the data proposed for collection during the RI is for risk management purposes. The results of the RI sampling and risk assessment activities will support the development and evaluation of appropriate remedial alternatives that address the estimated risks from exposure to Tittabawassee River sediments, floodplain soils, and Midland soils as needed. If the RI identifies unacceptable human health or ecological risks from sediments, the feasibility study will evaluate in situ remedial alternatives such as capping, monitored natural attenuation, institutional controls, hybrid approaches, and ex situ remedial alternatives such as dredging and excavation. Combinations of such approaches may be likely. *See* U.S. EPA, *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (December 2005) ("Contaminated Sediment Guidance"). Similarly, general remedial alternatives for floodplain soils determined to present an unacceptable human health or ecological risk will include excavation, river bank stabilization, engineered containment technologies, exposure barriers, monitored natural attenuation, and institutional controls. As with sediments, combinations of such remedial approaches are likely, tailored to the particular circumstances of each area (such as contaminant concentration, present and reasonably anticipated land use, potential for human or ecological exposure, estimated risk, habitat quality, mobilization potential, and similar conditions). The purpose of the RI is to gather the information necessary to evaluate site-specific risks and circumstances, including all of the elements listed in R 299.5528(3).

3. Conceptual Site Models

On February 23, 2006, Dow supplemented the originally submitted RIWPs with Conceptual Human Exposure Models in response to the receipt of MDEQ's verbal comments regarding exposure pathways. A copy of the Conceptual Human Exposure Models is provided in Attachment C. See also the attached exposure study plans (Attachment F) and response to Comment 16, which address the potential human exposure pathways for which site-specific data can be gathered beginning this year.

4. Potential Constituent of Interest/Target Analyte Identification

Attachment D is a Memorandum that supplements the original RIWPs. The Memorandum provides additional explanation for the selection of particular chemicals for evaluation. The list of TAs for the River will be finalized in a cooperative effort with MDEQ, and will be specifically discussed in the GeoMorph™ SAP. All available data from caged fish studies will be taken into account in developing this list.

The TA list for Midland will be modified as appropriate by the results of any on-site sampling MDEQ may conduct prior to the implementation of the revised *"Sampling and Analysis Plan in Support of Bioavailability Study"*.

5. Soil Sampling

The response to the soil sampling comments will be addressed in the Ann Arbor Technical Services (ATS) approach. A description of this approach is attached (Attachment A), along with the components and how the detailed work plan will be developed. Dow will propose an approach to sampling Priority 2 residential properties in conjunction with the Priority 2 IRA and in support of the RIWP. The Priority 2 IRA Soil will also include a proposal to include sampling on Priority 1 properties. It is anticipated that this Priority 2 sampling approach, which is incorporating elements of the GeoMorph™ approach, should be submitted to MDEQ by June 1, 2006.

The GeoMorph™ SAP will propose systematic, transect-based sampling oriented to the geomorphic features of the river and its floodplains. The appropriate floodplain boundaries will be developed in cooperation with MDEQ as part of the effort to develop that SAP. Aerial photography to produce detailed environmental topographic mapping for the entire area of interest will be collected. The sampling density in the GeoMorph™ SAP will be based on geomorphic complexity of the various reaches of the Tittabawassee River itself, and not on random or arbitrary grid spacing or vertical sample intervals and will be substantially greater than that proposed in the RIWP. The exact sampling locations will be developed in a cooperative effort with MDEQ.

GeoMorph™ concepts, including geomorphic mapping and GeoMorph™-caliber sample collection procedures for terrestrial soils, are currently being integrated into the sampling plans for IRA Priority 1 and Priority 2 areas. This will allow information developed for the IRAs and the GeoMorph™ river project to be used interchangeably. Field-verified geomorphic mapping of the Priority 1 and Priority 2 areas will be available in time to support sampling of those areas in 2006. It is anticipated that this Priority 1 and 2 sampling approach, which is incorporating elements of the GeoMorph™ approach, should be submitted to MDEQ by June 1, 2006.

6. Geospatial Modeling

Geospatial modeling will not be used to predict contaminant distribution. The GeoMorph™ process results in an empirical, "weight of evidence" site model. Geostatistics will be used to verify the adequacy of the empirically-derived site characterization.

7. Sediment Sampling

The GeoMorph™ investigation process is built upon a foundation that chemical contaminant distribution in riverine settings is the result of contaminant release specifics, and subsequent fate and transport processes. GeoMorph™ investigation strategies presume that the contaminant distribution is not random, and can be accurately and efficiently discerned by taking into account appropriate environmental factors such as erosion, transport, deposition, and contaminant chemistry.

See Attachment A for the ATS GeoMorph™ approach.

9. Mapping and Sampling of Erosional Areas

See the attached ATS approach in Attachment A. Identification of erosional and depositional areas, including erosional areas of the river banks, is fundamental to the GeoMorph™ process. These areas will be systematically identified and mapped over the entire 22 mile area of interest for the Tittabawassee River and its floodplains.

10. Midland Sampling

As MDEQ has acknowledged, the January 17, 2006 "*Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study*" (Support Study) is not part of the Midland RIWP, but rather is a pre-RI study that is being performed to provide data that can be used in conjunction with a full scale bioavailability study, if such a study is conducted. This pre-RI study is not intended to be part of or replace the RI; nevertheless, the proposed timeline for this study has been incorporated into the revised RI schedules because it is anticipated that the Support Study will provide data that will assist in the planning and design for future soil sampling for the City of Midland Study Area.

Dow understands that this comment is directed at the sampling described in the *Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study (CH2M HILL 2006)*. Dow and MDEQ met on April 20, 2006 to discuss proposed revisions to the sampling and analysis plan and are in fundamental agreement to a sample design utilizing samples randomly collected from approximately 300 foot by 300 foot boxes located along radial transects. A memorandum describing the agreed upon approach and process will be separately provided to the MDEQ on May 1, 2006. The proposed path forward for implementation of the sampling and analysis plan generally consists of: 1) meeting

with MDEQ by May 15, 2006 to finalize the proposed sampling locations and resolve the details of specific sampling protocols, 2) submission of a revised "*Sampling and Analysis Plan in Support of Bioavailability Study"* to MDEQ incorporating the agreed-upon changes by June 1, 2006; and 3) potential submittal of the MDEQ-approved plan to an independent scientific advisory panel (ISAP) for review and comment.

The revised work plan will address the issues raised by MDEQ and the comments raised by other NOD commenters referenced below.

11. Data Quality Objectives

Revised data quality objectives for the GeoMorph™ Investigation of the River Study Area will be identified in formal project QAPP revisions, prepared in cooperation with MDEQ. The project QAPP will be updated as necessary and appropriate when additional procedures or techniques are required.

The data quality objectives for the Midland Study Area will be revised, if necessary, in conjunction with the detailed soil sampling plan which will be developed after the development of the area wide cleanup criteria.

16. Exposure Data Collection

As referenced in the April 13, 2006 NOD, representatives of Dow, MDEQ, MDCH, MDA, US EPA, and the Saginaw-Chippewa Tribe have met on several occasions to discuss exposure issues and needs related to the planned site-specific HHRA. The exposures of interest for which site-specific information can be collected are illustrated by the Conceptual Human Exposure Models submitted to MDEQ on February 23, 2006, a copy of which is attached (Attachment C). These discussions clarified that many of the relevant exposure pathways lack site-specific data needed to properly conduct a site-specific HHRA. This will allow initial focus on the collection of site-specific data for all of the exposure pathways assigned a priority of 1 in the tables referenced in MDEQ's April NOD (with one exception) as part of the first phase of the RI. However, Dow does not agree that there was complete consensus on all aspects of the exposure pathway discussions.

The site-specific human exposure data needed can be divided into two broad categories: 1) Site-Specific Behavioral Data and 2) Site-Specific Exposure. Many risk assessments utilize assumptions regarding human exposure that may or may not be relevant to the situation at hand. These include assumptions on contact rates, as well as frequency and duration of various activities that bring humans into contact with contaminated media of one type or another.

Site-Specific Behavioral Data Collection

Activity Survey

Behavioral data will be collected to address exposure aspects in which normal or expected activities have the potential to bring humans into contact with contaminated environmental media. These data will be collected using an Activity Survey, which will elicit information from Study Area residents and visitors that allows quantification of certain exposure parameters. This survey will take the form of a retrospective, closed-ended questionnaire administered to a large section of the local Midland and Tittabawassee River populations and a prospective exposure diary kept by a subset of the same population to validate the results of the questionnaire. The questionnaire and diary format will be developed and pilot-tested in conjunction with MDEQ. The Activity Survey will elicit quantitative information on time spent indoors and outdoors at home and work by season; time spent engaged in activities that bring individuals into contact with soil or sediment by season; time spent in recreation by season; time spent fishing or hunting along with species collected, preparation methods, and rate of ingestion; use of homegrown fruits, vegetables, meats, eggs and milk, preparation methods, and rate of ingestion; and specific cultural activities that may increase contact with contaminated media.

Dow will consult with representatives of the Saginaw-Chippewa Tribe to ensure that any unique tribal exposure issues are included and accurately represented as a module of the Activity Survey, and to determine how best to administer the survey to tribal members who reside in or otherwise visit the River Study Area.

The Activity Survey will provide quantitative measures of various land use specific exposures. As an example, residents along the river might be found to spend an average of 16 hours per week outdoors on their property during the summer (based on the range, standard error and shape of the distribution from the responses received). Such information will be combined with other aspects of the exposures identified to develop the site-specific Probability Density Functions (PDFs) that will be used in the exposure assessment portion of HHRA.

Site-Specific Exposure Studies

The data collection pursuant to the Site-Specific Exposure Study Plans will provide the Exposure Point Concentrations (EPCs) or Concentration Terms that are required to estimate exposure and ultimately human health risk. These Study plans will be finalized in terms of location, sample type and numbers, and sample preparation issues in consultation with MDEQ. The attached proposed Site-Specific Exposure Study plans include

1) Fish Tissue Study Plan – identification of TAL concentrations in the tissue of Tittabawassee River fish consumed locally and prepared in a manner consistent with the practices of local fishermen.
2) Game Tissue Study Plan – identification of TAL concentrations in the tissue of wild game consumed locally and prepared in a manner consistent with the practices of local hunters.
3) Domestic Livestock Sampling Plan – identification of TAL concentrations in the tissue of livestock, dairy or egg products raised and consumed locally and prepared in a manner consistent with the practices of local consumers.
4) Garden Vegetable Study Plan – identification of TAL concentrations in the tissue of garden crops raised and consumed locally and prepared in a manner consistent with the practices of local consumers.
5) Stationary Airborne Agricultural Dust Study Plan – identification of TAL concentrations in the dust raised as the consequence of normal agricultural activity and which may be potentially inhaled by neighboring residents.
6) Personal Airborne Dust Exposure Study Plan – identification of TAL concentrations in the dust raised as the consequence of normal agricultural activity and which may be potentially inhaled by farmers during such activity**.**

Based on the importance of the Activity Survey, the level of effort and the length of time required to develop and implement it, the Activity Survey has the highest priority of the Site Specific Study plans. Since information derived from the Activity Survey also informs aspects of certain other Study plans (for instance, the type of fish or game and the manner of preparation), it must be implemented in advance of those study plans. Exposure data collection activities will be prioritized and implemented as follows; however, certain activities can only take place at certain times of the year (e.g., vegetable gardens, farming activities) and/or require time to adequately complete so the final implementation will be based on the approval and seasonality issues.

1) Soil and Sediment Sampling data for the HHRA will be obtained as part of the GeoMorph™ SAP nature and extent evaluation activities of the RIWP. Attachment H discusses how the data obtained from the field investigations will be evaluated for incorporated into the HHRA.
2) Airborne Agricultural Dust Sampling can begin during the fall harvest once the farms in question have been located, property access has been granted, and the sampling plan has been approved.
3) Personal Dust Inhalation Sampling can also begin during the fall harvest once the farmers needed have been recruited and the sampling plan has been approved.
4) Garden Vegetable Sampling can occur during the present growing season if the sampling plan is approved, relevant data from the Activity Survey are available, gardens are identified, and access to the crops is granted before the crops ripen.

5) Domestic Livestock Sampling can begin at any time once the sampling plan is approved, relevant data from the Activity Survey is available, properties with livestock identified, and access to the livestock, milk, or eggs is granted.
6) Fish Tissue Sampling in the Tittabawassee River can begin once the sampling plan is approved, relevant data from the Activity Survey is available, and the appropriate fishing season has arrived.
7) Game Tissue Sampling can begin once the sampling plan is approved, relevant data from the Activity Survey is available, and the appropriate hunting season (fall) has arrived.

Draft Study plans are attached to this response.

Response to April 13, 2006 Notice of Deficiency

Attachment 1

2. Congener-specific Results

The following studies were conducted by Dow prior to the submission of the RIWPs and contained dioxin/furan analyses.

Tittabawassee River Floodplain Scoping Study Field Investigation Report, *CH2M HILL, December 2005. This report was provided as Appendix B for the TR RIWP. Dioxin/furan TEQ results for the scoping studies were provided in Appendices E and F of the TR RIWP. Dioxin/furan congener-specific data from the scoping studies was provided prior to the submission of the TR RIWP in the 2nd and 3rd Quarter 2005 Environmental Monitoring Reports provided to MDEQ.*

Tittabawassee River Sediment Vertical Variability, *CH2M HILL, July 2005. Dioxin/furan congener-specific results were provided in Appendix C, Table C-1 of this report.*
Tittabawassee River Sediment Dioxin/Furan Concentration Variability, *CH2M HILL, March 2005. Dioxin/furan congener-specific results were provided in Appendix C, Table C-1 of this report.*

Ecological Risk Assessment Support Sampling, *CH2M HILL, March 2005. Dioxin/furan TEQ results were provided in Tables 1 and 2. A compact disk was provided along with the report that contained all analytical data, including the congener-specific results for dioxin/furan analyses.*

Dow did not conduct any studies in the Midland area involving the collection of samples for dioxin/furan analyses prior to submission of the MS RIWP. Information from historic studies was previously provided to MDEQ.

3. Analytical Data Comparison

See Attachment G for the methods Dow utilizes to validate data obtained from commercial laboratories.

4. Tittabawassee River Bioavailability Support Soil Sampling Clarification

With the geomorphic approach being proposed for the Tittabawassee River and Floodplain, Dow is revising its initial approach for the determination of soil bioavailability parameters as described in the December 29, 2005 RIWP submittal. The collection of samples to determine the soil types to be used for a potential bioavailability study will be integrated into the geomorphic sampling plan. This approach will allow samples to be collected from geomorphic features being studied where other data will also be collected and will include various land uses (including residential properties). This will allow the final soil selection for the potential study to be made from areas of known impact and be directly related to the land use.

Attachment 2

2. PCOI/TAL

See the response to the March NOD item # 4, above. The TAL will be finalized in a cooperative effort with MDEQ, and will be specifically discussed in the GeoMorph™ SAP. All available data from caged fish studies will be taken into account in developing this list.

3. Geospatial Modeling: Sediment and Soil Sampling

See the response to the March NOD item #s 3, 5, 6 & 7 and Attachment A.

8. Sediment Sampling

See the response to the March NOD item #s 5 and 7, above and in Attachment A.

9. Exposure Pathways

See the response to the March NOD item #16, above. The Activity Survey Study Plan, Attachment E, will include the development of questions intended to identify whether the "special residential cultural/Native American" exposure pathways, referenced in the comment, are present along the River and in the City of Midland.

Attachment 3

4.e. Distribution

See the response to the March NOD item # 7, above and Attachment A.

4.f. Sampling of Residential and Agricultural Properties

See the response to the March NOD item # 5, above and Attachment A.

6. Residential Sampling

See the response to the March NOD item # 5, above and Attachment A.

Attachment 4

3.d. Adequacy of Sampling Data

When Dow proposes the detailed RI sampling plan for Midland as indicated in the revised schedule it will address the issue raised by the commenter in reference to dioxin and any other TAs.

3.e. Third Party

See the response to the March NOD item #10 which clarifies that this proposed sampling is not part of the RIWP. This comment will be incorporated into the design of the revised "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study"*. On May 1, 2006 a summary of the agreed approach and process will be submitted followed by a revised work plan on June 1, 2006.

3.f. Sample Retention

This comment will be addressed as part of the revisions to the "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study (CH2M HILL 2006)*" which will be submitted to MDEQ on June 1, 2006 since this plan includes the collection of samples that will held, but not analyzed, unless a reported result exceeds a specific predefined action level. Holding of samples was not a component of the MS RIWP.

3.g. Blinding of Sample Locations

See the response to the March NOD item #10 which clarifies that this proposed sampling is not part of the RIWP.

Dow understands that this comment is directed at the sampling described in the "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study (CH2M HILL 2006)"*. Dow and MDEQ met on April 20, 2006 to discuss proposed revisions to the sampling and analysis plan that included provisions to protect the anonymity of private property owners. This approach will be described in the May 1, 2006 memorandum and will be incorporated into the revised sampling and analysis plan which will be submitted under on June 1, 2006.

4. Quality Assurance

A Quality Assurance Project Plan (QAPP) and Standard Operating Procedures (SOPs) were previously submitted to MDEQ and EPA for review and comment. These plans provide standards of practice by which the Dow's RI program will be implemented and ensure that the methods follow standard practices. In addition, sampling and analysis plans are submitted to MDEQ for approval for various activities. Through the review and approval process, MDEQ and EPA have the opportunity to request or require different methods. Finally, MDEQ and EPA could decide to collect split samples during sampling activities. These plans will be appropriately revised as needed as new procedures and techniques are identified.

4. b. Blinding of Samples

See the response to the March NOD item #10 which clarifies that this proposed sampling is not part of the RIWP.

As previously noted, The "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study (CH2M HILL 2006*)" will be revised in response to NOD comments and in accordance with the outcome from the Dow and MDEQ meeting on April 20, 2006. During this meeting, Dow and MDEQ agreed on proposed provisions to protect the anonymity of private property owners and criteria under which results would be revealed. This approach will be described in a memorandum that will be submitted on May 1, 2006 and will be incorporated into the revised sampling and analysis plan to be submitted on June 1, 2006.

5. b. Request for Sampling Information

See the response to the March NOD item #10 which clarifies that this proposed sampling is not part of the RIWP.

Information on how property owners can obtain information about samples collected on their property will be included in the revised Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study and will be described and provided again to the property owners when Dow contacts them to request access for sampling.

5.c. Protection of the Identify of Sample Requesters

See the response to the March NOD item #10 which clarifies that this proposed sampling is not part of the RIWP.

The revised "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study"* will indicate that neither MDEQ nor Dow can obtain information on property owner requests from the third party.

13. Sampling Density

The revised Midland RI schedule indicates that the initial sampling for purposes of conducting the RI in Midland will take place following the analysis of data from the revised "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study"* and following the development of alternative criteria as set forth in the Framework for an Agreement. The RI sampling approach and design will be based on the available data about dioxin concentrations as well as the presence of other TAs, if any, and the applicable criteria.

The MS RIWP will be a phased process that is specifically designed to provide sufficient information for making remedial decisions while at the same time minimizing the disruption to the residents and obtaining sufficient characterization data in as short a timeframe as possible. The PreRI sampling to be conducted under the revised "*Sampling and Analysis Plan in Support of Bioavailability Study"* will be used to develop and focus the Phase II sampling required to complete the characterization of the Midland Study Area.

14. Sampling of Residential Property

Residential soil samples will be collected as part of the pre-RI Support Sampling that will be conducted under the revised "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study"*.

Dr. David Garabrant of the University of Michigan has reported that the University of Michigan Dioxin Exposure Study (UMDES) results will be reported in mid-August, 2006. Based on the University's study protocol, it is expected that the study will report on household dust concentrations. It is possible that the study may report household dust concentrations in relationship to outdoor soil concentrations and with respect to blood levels. This information will be considered in evaluating the relevance of household dust as a relevant exposure pathway and thus, as a pathway that merits site specific data collection.

It is our understanding from the UMDES protocol that when the University of Michigan (for its large Exposure Study) and the Michigan Department of Community Health (for

the limited Pilot Exposure Investigation) collected household dust samples, they sampled areas of frequent use and therefore high potential for contact and did not sample dust in unused or infrequently used areas of the residences that are difficult to access. Media reports indicate the commenter's reference to information about attic dust in West Virginia was information collected on behalf of an attorney representing private parties for a potential lawsuit. It is not clear to us that either the West Virginia Department of Environmental Protection or EPA considered that this information had any particular scientific merit or took any action as a result.

15. Sampling Design

As referenced in the response to comment 13, above, the detailed design of the RIWP sampling will take into consideration the data obtained from the Support Sampling as well as data reported by the University of Michigan Dioxin Exposure Study.

One of the primary objectives of the MS RIWP is to collect information to characterize the lateral and vertical distribution of TAs released from the Dow Midland Plant into offsite areas. Releases may have occurred over the life of the facility and are not limited to any one particular source. The sampling design in the RIWP consists of a phased process designed to evaluate the presence or absence of TAs in the Midland area that originated from the Dow Midland Plant, regardless of their source. This includes consideration of emissions from incinerators, powerhouses, process units, fugitive dust, etc. Sampling results from the "*Midland Area Soils Sampling and Analysis Plan in Support of Bioavailability Study"* will be used to help guide future sample planning and will be incorporated into the revised MS RIWP.

Attachment A
Sampling and Analysis Plan Development Overview
Tittabawassee River

A. Developmental Process

A collaborative process will be used by the *GeoMorph*™ team and Michigan Department of Environmental Quality (MDEQ) to develop the Sampling and Analysis Plan (SAP) for the Tittabawassee River. Together, each group will commit to project schedules, establish a platform for open dialog among technical and management representatives, and tap collective views to generate consensus, result-based solutions.

To foster the collaborative process and build consensus project documents, iterative "working sessions" are planned to bring technical representatives from the *GeoMorph*™ team and MDEQ together either by teleconference/NetMeetings and/or informal face-to-face meetings. Working sessions will be used to foster dialogue, clarify areas of agreement and disagreement, improve the information upon which decisions are based, and resolve issues in ways that both groups find acceptable. Working sessions will involve core technical members from each group with the goal of gaining early participation, collaboration, and consensus prior to submittal of project documents for final agency approval.

The following tentative schedule was developed to facilitate the collaborative process and work though *GeoMorph*™ SAP components 1 though 10, in the following section:

May 11, 2006 - MDEQ/GeoMorph Team Working Session #1
May 16, 2006 - Draft - GeoMorph SAP
May 18, 2006 - MDEQ/GeoMorph Team Working Session #2
May 24, 2006 - Second Draft - GeoMorph SAP
May 26, 2006 - MDEQ/GeoMorph Team Working Session #3
June 1, 2006 - Submit GeoMorph SAP to MDEQ
June 30, 2006 - MDEQ Approval GeoMorph SAP
July 10, 2006 - Commence GeoMorph SAP Field Activity

B. SAP Approach and Layers

The *GeoMorph*™ process consists of a series of environmental tools to address erosion, transport, deposition, and the contaminant environmental fate and effects. It is used to identify areas of sediment deposition and erosion based on river characteristics (gradient, water velocity, thalweg location, river sinuosity, and morphology of floodplain and terraces). It identifies similar sediment deposition areas and focuses sampling to characterize these units. The general process layers include:

1. High Resolution Topographic Mapping: High resolution topographic mapping is required with 1 foot surface contours. This mapping is used to help establish the longitudinal profile, river reaches, and serves as the base layer for the geomorphic site model.

2. Longitudinal Profile: The purpose of the longitudinal profile is to determine changes in the channel gradient along the river. Changes in channel gradient have an affect on sediment deposition patterns throughout the river system.
3. Geomorphic Characteristics: Geomorphic characteristics of the river are established and include: channel width, channel depth, water velocity, thalweg, sinuosity, river discharge, channel bottom slope, channel bed roughness, sediment load, and sediment size. The purpose of the geomorphic characterization is to establish the depositional patterns within the river and understand the transport and storage of contaminated sediments.
4. Reach Determination: Changes in channel gradient provide information about the reaches of the river. Channel gradient, channel width, channel bed material, and sinuosity are used to determine the reaches of the river. A river reach is a section of the river with a similar channel slope, channel width, channel bed material, and sinuosity. Reaches are important because depositional patterns on like-geomorphic surfaces will be similar within a given reach.
5. Target Analyte List and Release Summary: Target Analyte (TA) List and Dow historical release information will be completed for the Tittabawassee River. Over-laying the release timelines to the extent such information is available, will provide an important element in understanding the distribution of TAs in the in-channel sediments and floodplain soils. See the Technical Memorandum regarding PCOIs/TALs (Attachment D).
6. Aerial Photographic and Anthropogenic Influences Analysis: Historical aerial photograph review is conducted to identify modification to the river system, both man-made and natural. Particular attention is given to those modifications that affect the extent of lateral movement of the river during the time period of contaminant release. This historical perspective provides insight on the changes to the deposition and erosion pattern of the river. It is used to focus the sampling investigation on the areas of historic sediment deposition for the time period since the contaminant release.
7. Characterization of Fluvial Processes: A thorough understanding of the forces and processes responsible for the exchange of TA impacted solids in the river system is essential in the development of a scientifically sound remedial investigation. This information is fundamental in understanding the movement and mobility of solids in the river system. It is required to properly characterize erosion/deposition areas so that exposure risk can be properly evaluated, and to establish the confidence level about the predictability of the geomorphic model.
8. Geomorphic Surface Mapping: Preliminary geomorphic surface mapping is conducted using the reaches of the river and the detailed topographic mapping to identify the geomorphic surfaces of the river. Geomorphic surfaces typically include in-channel deposition areas, in-channel erosion areas, floodplain, low terraces, intermediate terraces, high terraces and upland. The deposition patterns are subsequently confirmed by a detailed soil profile analysis during the field confirmation sampling.
9. Geomorphic Mapping/Field Confirmation: The field confirmation process is used to review, evaluate, and confirm or revise the findings of the preliminary geomorphic surface mapping. The confirmation process involves visual

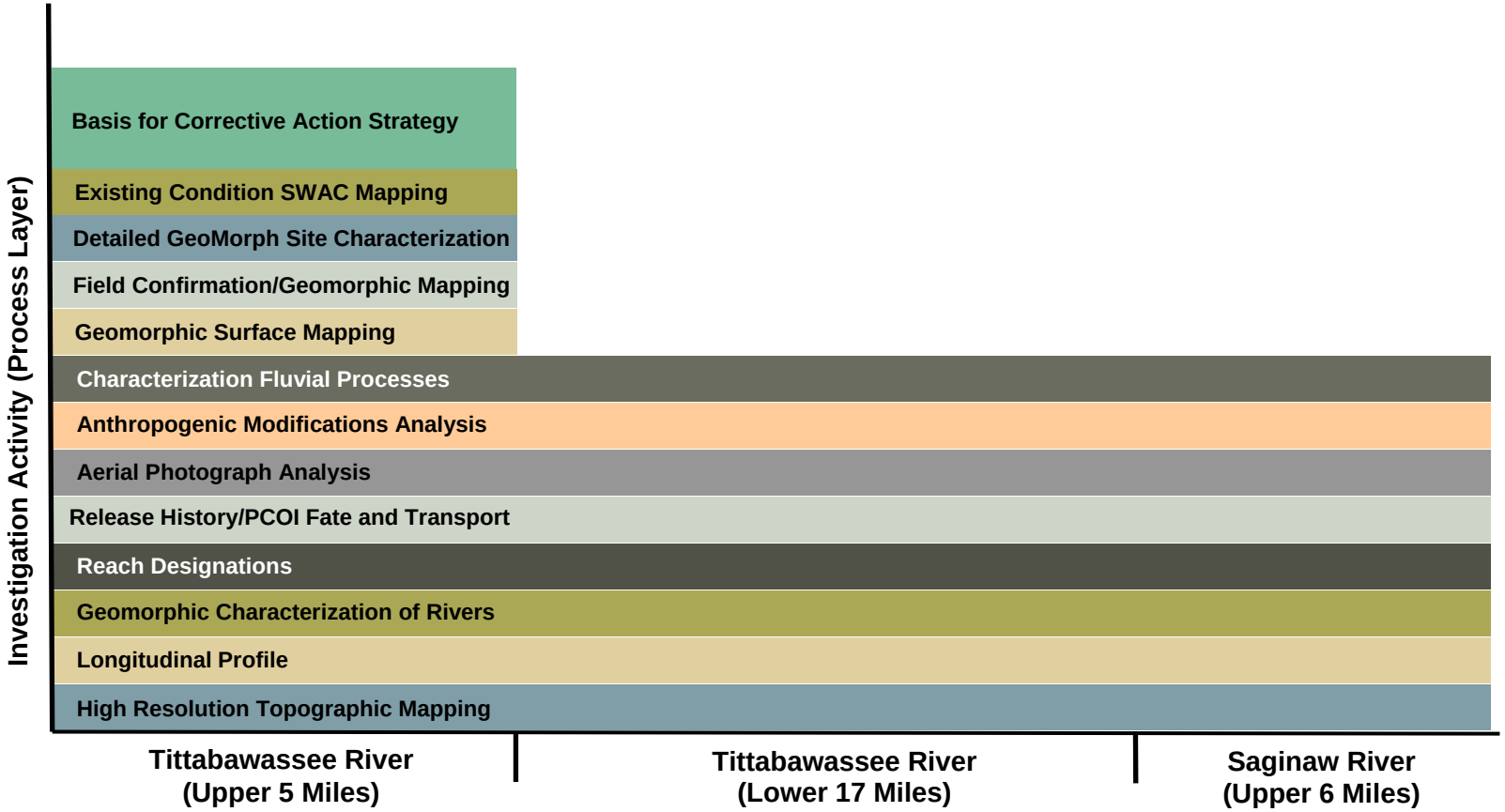
observation and mapping/data collection/photographs of the river flow characteristics, the channel bank, channel bed material, review of historic deposition areas, and confirmation/changes to the geomorphic surfaces. The results of the field confirmation build on the previous layers and provide the basis for the detailed *GeoMorph*™ site characterization.

10. Develop *GeoMorph*™ SAP: A detailed geomorphic-based SAP will be developed to characterize the sediments and soils along the Upper Tittabawassee River. Data collection activities proposed in this SAP will provide a detailed *GeoMorph*™ site characterization of the river, sufficiently comprehensive to evaluate risk and corrective action strategies.
11. Detailed *GeoMorph*™ Site Characterization: Implementing the SAP will complete the characterization of the sediments and soils along the Upper Tittabawassee River, from the confluence of the Chippewa and Tittabawassee Rivers downstream approximately six miles (Reaches A though N, Stationing 0+00 through 330+00).
12. Existing Condition GeoMorph Surface Weighted Average Concentration (SWAC) Analysis: An existing condition SWAC model will be developed based on geomorphic polygons for "like areas" and incorporating the chemistry data for PCOI along with erosion factors and other factors for each polygon. The existing condition SWAC provides a basis for evaluating risk and corrective action strategies.

C. Summary of 2006 Activities

See Figure 1.

Figure 1
Summary of Activities: 2006

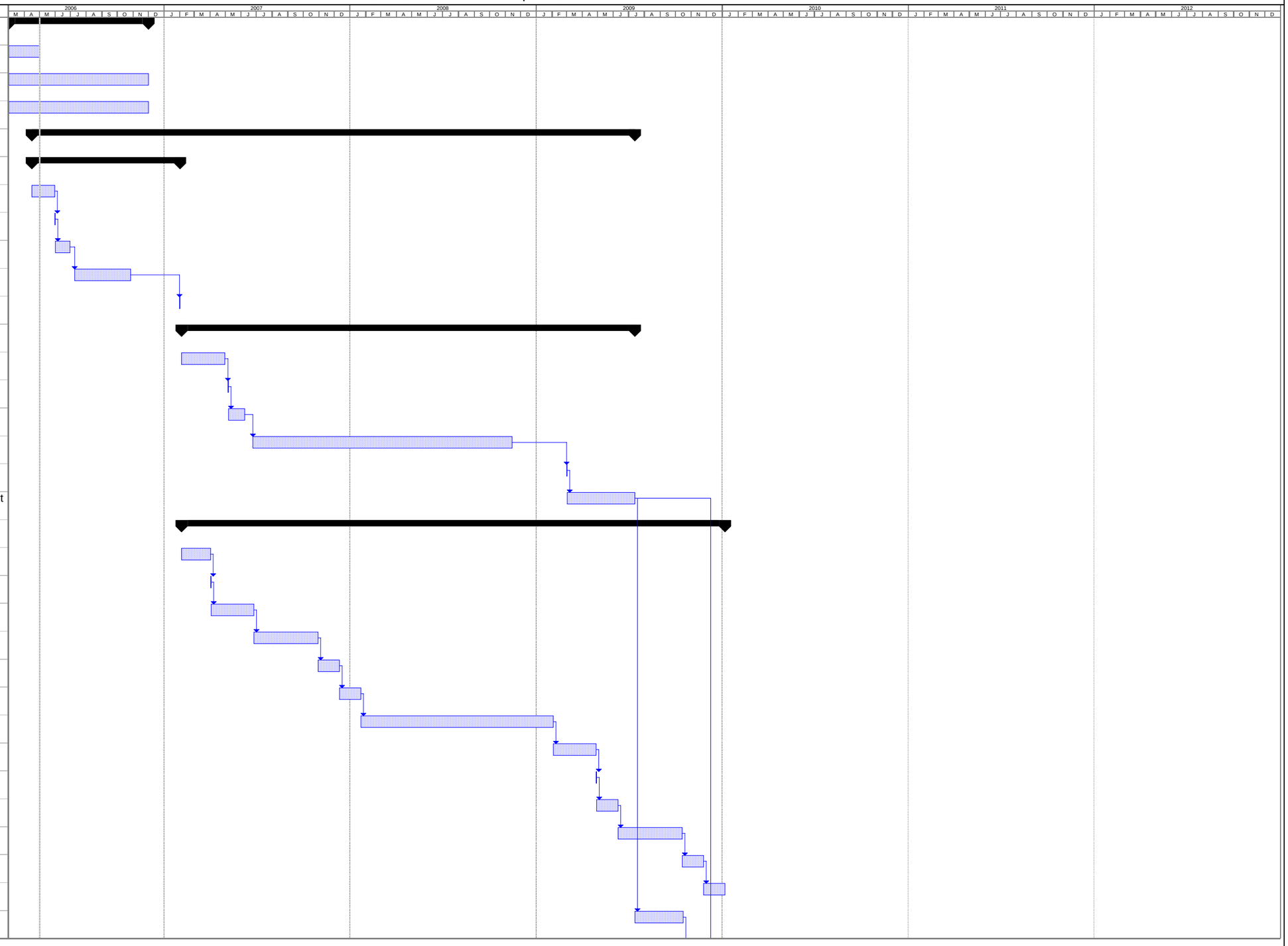


Attachment B

Revised Tittabawassee River and Midland Area RIWP Schedules

Tittabawassee River & Floodplain Schedule

ID	Task Name
1	**Tittabawassee River**
2	Notices of Deficiency First Response
3	Notices of Deficiency Second Response
4	Revised Schedule Incorporating HHRA Process
5	**Remedial Investigation**
6	**GeoMorph Phase I**
7	GeoMorph Phase I SAP Development
8	GeoMorph Phase I SAP Submittal to MDEQ
9	MDEQ Review and Approval of GeoMorph Phase I SAP
10	GeoMorph Phase I Field Activity
11	GeoMorph Phase I Site Characterization Report Submitted to MDEQ
12	**GeoMorph Phase II**
13	GeoMorph Phase II SAP Development
14	GeoMorph Phase II Submittal to MDEQ
15	MDEQ Review and Approval of GeoMorph Phase II SAP
16	GeoMorph Phase II Field Activity
17	GeoMorph Phase II Site Characterization Report Submitted to MDEQ
18	MDEQ Review and Approval of Site Characterization Report
19	**Full Bioavailability Study**
20	Development of Bioavailability Study Plan
21	Submittal to MDEQ of Draft Bioavailability Study Plan
22	MDEQ Review of Draft Bioavailability Study Plan
23	Science Advisory Panel Review of Draft Bioavailability Study Plan
24	Finalize Work Plan
25	MDEQ Approval of Final Bioavailability Study Plan
26	Implementation of Bioavailability Study Plan
27	Draft Report of Bioavailability Study Results Prepared
28	Draft Report of Bioavailability Study Results Submitted
29	MDEQ Review of Draft Bioavailability Study Plan Results
30	Science Advisory Panel Review of Draft Bioavailability Study Results
31	Final Bioavailability Study Results Prepared
32	MDEQ Review and Approval of Final Report
33	Feasiblility Study for Tittabawassee River

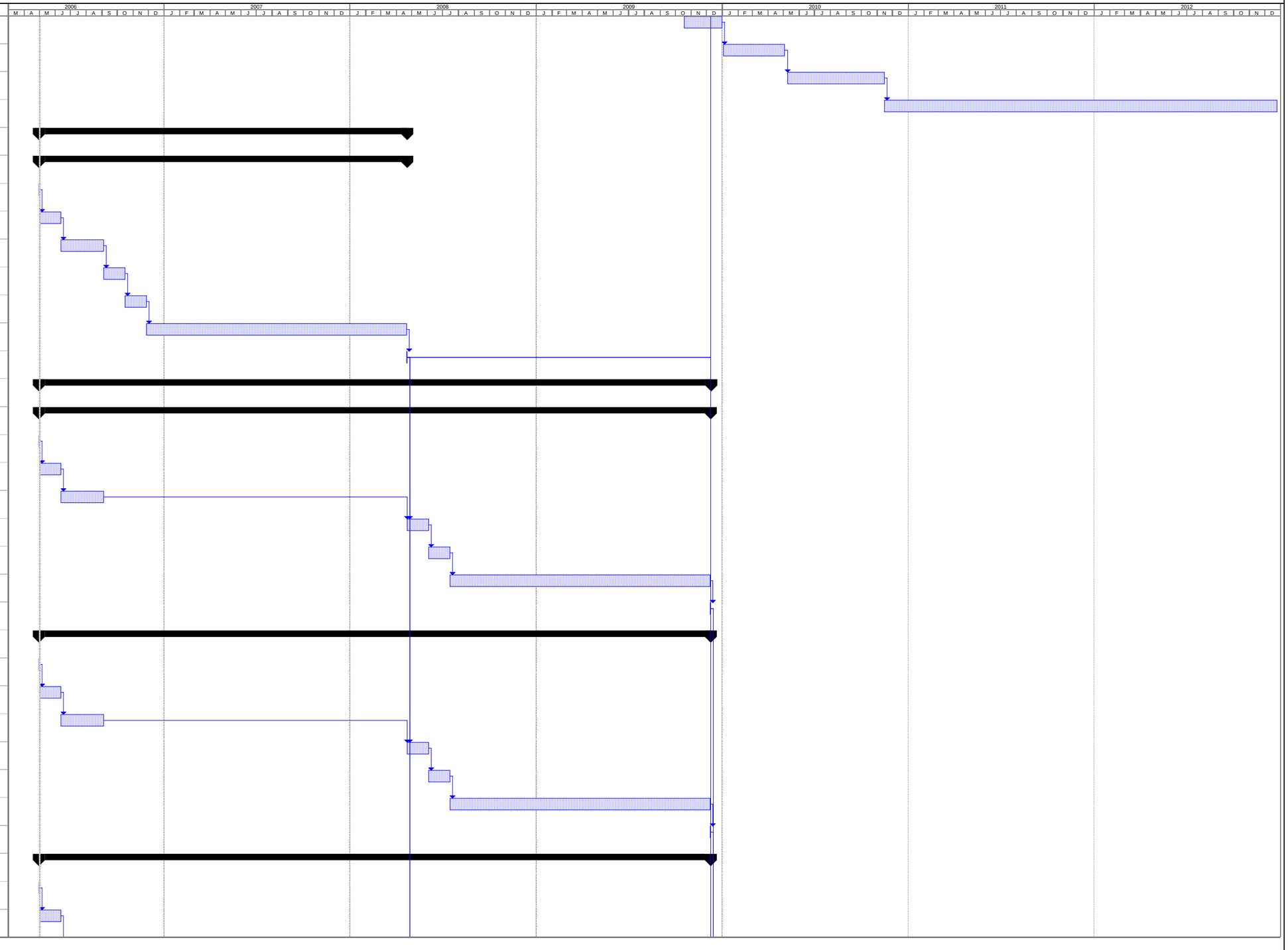


Tittabawassee River & Floodplain Sch
Date: Mon 5/1/06

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress | Split | External Tasks | Project Summary | Group By Summary | Deadline

Tittabawassee River & Floodplain Schedule

ID	Task Name
34	Remedy Evaluation
35	Remedy Selection
36	Remedial Design
37	Remedy Implementation
38	**Behavorial Study Plans**
39	**Activity Survey**
40	Study Plan Submitted
41	MDEQ Review
42	Science Advisory Panel Review and Comment
43	Finalize Study Plan
44	MDEQ Study Plan Approval
45	Study Plan Implementation
46	Final Report Submitted to MDEQ for Review and Approval
47	**Exposure Study Plans**
48	**Stationary Airborne Agricultural Dust Study**
49	Study Plan Submitted
50	MDEQ Review
51	Science Advisory Panel Review and Comment
52	Finalize Study Plan
53	MDEQ Study Plan Approval
54	Study Plan Implementation
55	Final Report Submitted to MDEQ for Review and Approval
56	**Personal Airborne Dust ExposureStudy Plan**
57	Study Plan Submitted
58	MDEQ Review
59	Science Advisory Panel Review and Comment
60	Finalize Study Plan
61	MDEQ Study Plan Approval
62	Study Plan Implementation
63	Final Report Submitted to MDEQ for Review and Approval
64	**Fish Sampling Study Plan**
65	Study Plan Submitted
66	MDEQ Review

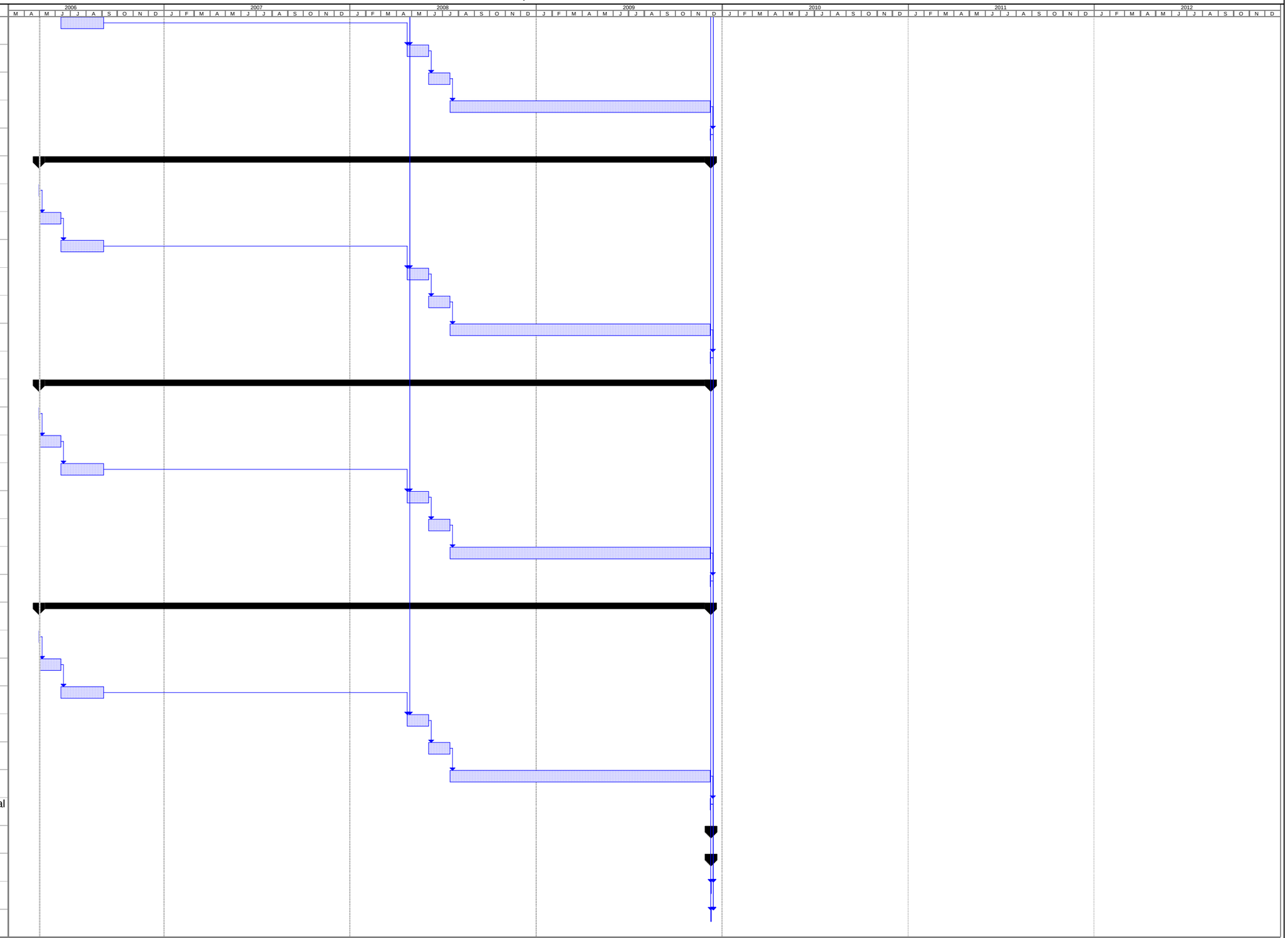


Tittabawassee River & Floodplain Sch
Date: Mon 5/1/06

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress | Split | External Tasks | Project Summary | Group By Summary | Deadline

Tittabawassee River & Floodplain Schedule

ID	Task Name
67	Science Advisory Panel Review and Comment
68	Finalize Study Plan
69	MDEQ Study Plan Approval
70	Study Plan Implementation
71	Final Report Submitted to MDEQ for Review and Approval
72	**Small Game Study Plan**
73	Study Plan Submitted
74	MDEQ Review
75	Science Advisory Panel Review and Comment
76	Finalize Study Plan
77	MDEQ Study Plan Approval
78	Study Plan Implementation
79	Final Report Submitted to MDEQ for Review and Approval
80	**Garden Vegetable Study Plan**
81	Study Plan Submitted
82	MDEQ Review
83	Science Advisory Panel Review and Comment
84	Finalize Study Plan
85	MDEQ Study Plan Approval
86	Study Plan Implementation
87	Final Report Submitted to MDEQ for Review and Approval
88	**Domestic Livestock Study Plan**
89	Study Plan Submitted
90	MDEQ Review
91	Science Advisory Panel Review and Comment
92	Finalize Study Plan
93	MDEQ Study Plan Approval
94	Study Plan Implementation
95	Final Report Submitted to MDEQ for Review and Approval
96	**Human Health Risk Assessment**
97	**HHRA Work Plan**
98	Development of Exposure Factors
99	Development of Toxicity Factors



Tittabawassee River & Floodplain Sch
Date: Mon 5/1/06

Task | Progress | Milestone | Summary | Rolled Up Task | Rolled Up Milestone | Rolled Up Progress | Split | External Tasks | Project Summary | Group By Summary | Deadline

TITTABAWASSEE RIVER & FLOODPLAIN SCHEDULE
ASSUMPTIONS

- Human Health Risk Assessment Work Plan cannot be developed until Notices of Deficiency HHRA responses have been prepared which is due on December 1, 2006. The timing in the schedule is considered a placeholder and will be updated with the December 1, 2006 submittal.
- Feasibility Study, Remedy Evaluation, Remedy Selection, Remedial Design and Remedy Implementation are placeholders. These cannot be reliably estimated until completion of site characterization and human health risk assessment.
- Science Advisory Panel times for reviews of selected study/work plans cannot reliably estimated at this time. The time will vary based upon the complexity of the study/work plan they are being requested to review and provide comment.
- Exposure Study Plan schedules are based upon the Target Analyte List (TAL) contained within the document. If other constituents are added to the TAL implementation of these work plans may be delayed until TAL is finalized.
- Soil characterization to identify soil types and sample locations for future Bioavailability Study will be integrated into the geomorphic approach for the Tittabawassee River.
- Science Advisory Panel review of various study plan will follow a complete and rigorous SAP review process
- Relevant Exposure Studies may not be initiated until Activity Survey has been completed and results reviewed by Science Advisory Panel and approved by MDEQ

Midland Soils Schedule

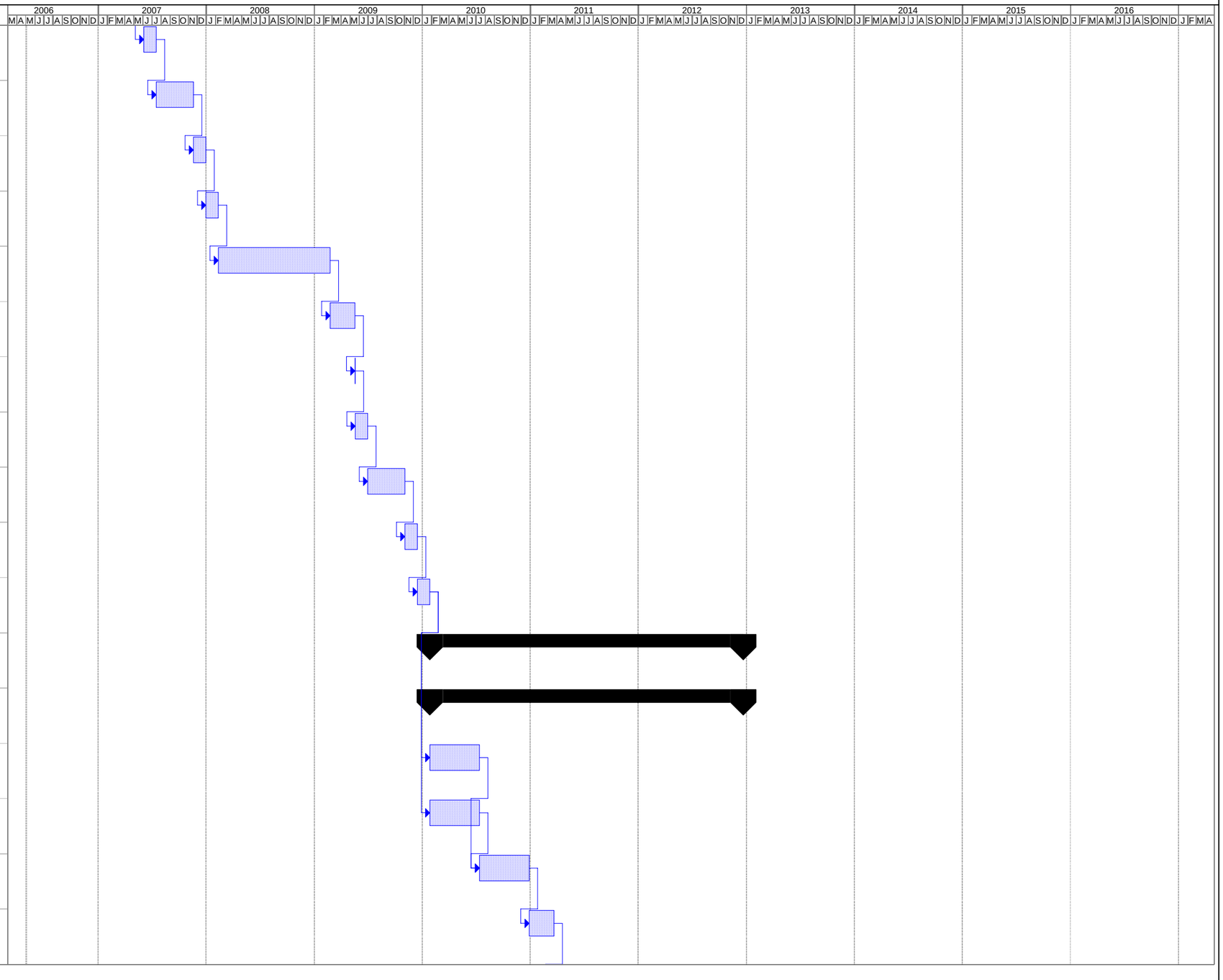
ID	Task Name
1	**Notices of Deficiency Responses**
2	NOD First Response
3	NOD Second Response
4	**Midland Pre-RI Soils**
5	Submittal of Memo Outlining PreRI Sampling Approach
6	Revised "Sampling Approach in Support of Bioavailability Study" Work Plan Developed &
7	Initiate obtaining access agreements for potential sampling locations
8	MDEQ review of PreRI Work Plan
9	Science Advisory Panel review of PreRI Work Plan
10	Finalize Work Plan
11	MDEQ final approval of PreRI Work Plan
12	Implementation of PreRI Work Plan
13	Draft Report Submitted to MDEQ
14	MDEQ Review and approval of PreRI Report
15	**Full Bioavailability Study**
16	Development of Bioavailability Study Plan
17	Submittal to MDEQ of Draft Bioavailability Study Plan

Midland Soils Schedule
May 1, 2006

Task | Split | Progress | Milestone | Summary | Project Summary | External Tasks | External Milestone | Deadline

Midland Soils Schedule

ID	Task Name
18	MDEQ Review of Draft Bioavailability Study Plan
19	Science Advisory Panel Review of Draft Bioavailability Study Plan
20	Finalize Work Plan
21	MDEQ Approval of Final Bioavailability Study Plan
22	Implementation of Bioavailability Study Plan
23	Draft Report of Bioavailability Study Results Prepared
24	Draft Report of Bioavailability Study Results Submitted
25	MDEQ Review of Draft Bioavailability Study Plan Results
26	Science Advisory Panel Review of Draft Bioavailability Study Results
27	Final Bioavailability Study Results Prepared
28	MDEQ Review and Approval of Final Report
29	**Human Health Risk Assessment**
30	**AWCC/SSCC Development Initiated**
31	Development of Exposure Factors
32	Development of Toxicity Factors
33	AWCC/SSCC Number Developed
34	AWCC Submitted for MDEQ Review

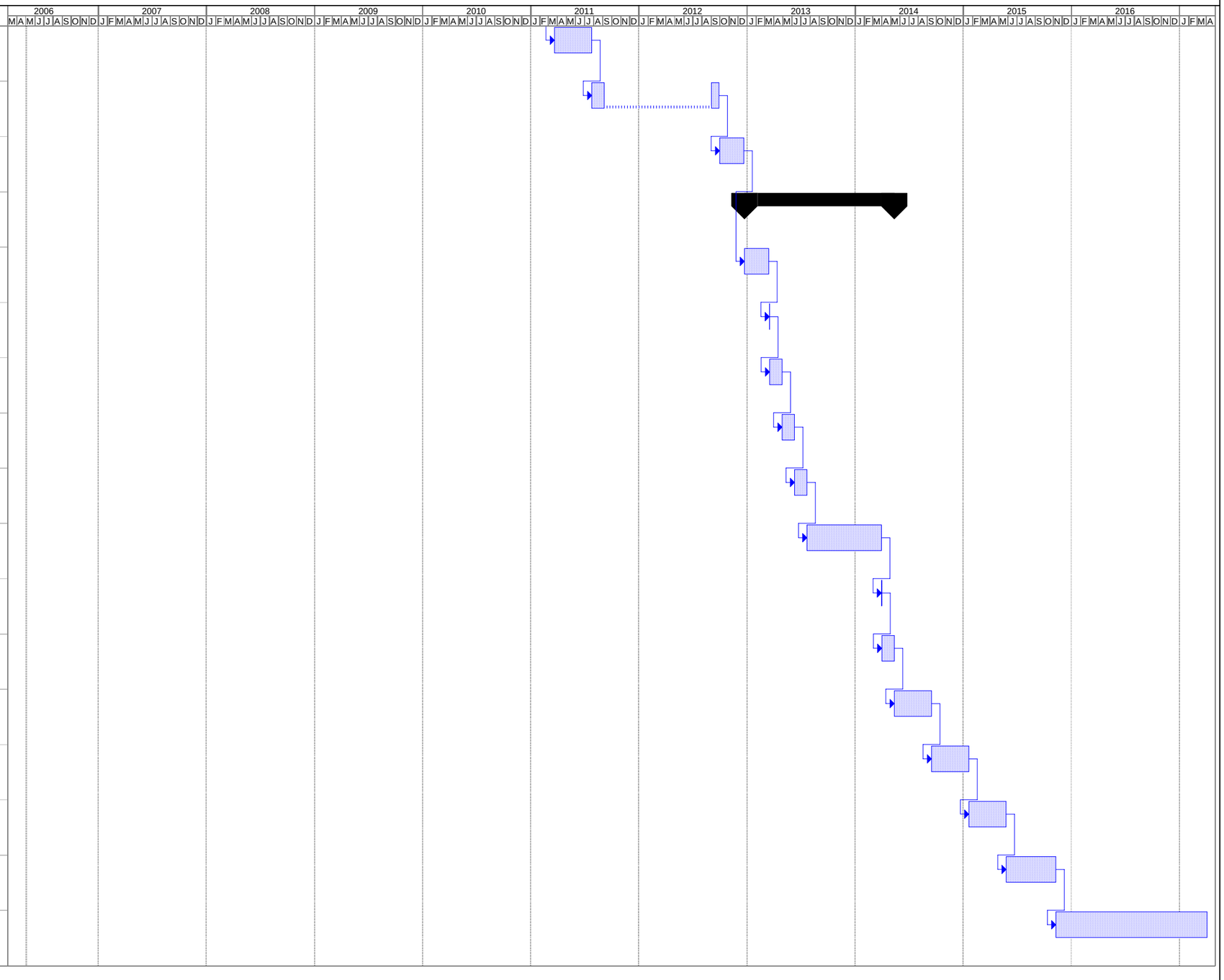


Midland Soils Schedule
May 1, 2006

Task | Split | Progress | Milestone | Summary | Project Summary | External Tasks | External Milestone | Deadline

Midland Soils Schedule

ID	Task Name
35	AWCC Review by Science Advisory Panel
36	AWCC Revised and Resubmitted to MDEQ
37	MDEQ Approval of Final AWCC Number
38	**Midland Soils Phase II**
39	Development of Phase II Sampling and Analysis Plan
40	Submittal of Phase II Sampling and Analysis Plan
41	MDEQ review and comment on Phase II Work Plan
42	Finalize Work Plan
43	MDEQ final approval of Phase II Work Plan
44	Implementation of Phase II Work Plan
45	Draft Report Submitted to MDEQ
46	MDEQ Review and approval of Phase II Report
47	Feasiblility Study for Midland Soils
48	Remedy Evaluation
49	Remedy Selection
50	Remedial Design
51	Remedy Implementation



Midland Soils Schedule
May 1, 2006

Task | Split | Progress | Milestone | Summary | Project Summary | External Tasks | External Milestone | Deadline

MIDLAND SOILS SCHEDULE
ASSUMPTIONS

- City of Midland will concur with Pre-RI sampling approach
- MDEQ and Dow will finalize locations of sample "boxes" at joint meeting in early May
- MDEQ will approve the revised "*Midland Representative Soils Sampling and Analysis Plan In Support of Bioavailability Study"* without significant changes within 30 days of submittal
- Science Advisory Panel review will focus on soil parameters, not sampling approach, and provide comments within 30 days
- Lab analysis will be completed using standard laboratory turnaround time
- Data validation to be completed in 21 days from receipt of laboratory data
- Field work will take approximately 6 weeks
- Full Bioavailability Study Plan will not be prepared until "*Midland Representative Soils Sampling and Analysis Plan In Support of Bioavailability Study"* PreRI Final Report has been approved by MDEQ
- Science Advisory Panel review of Full Bioavailability Study Plan will follow a complete and rigorous SAP review process
- Relevant Exposure Studies will not be initiated until Activity Survey has been completed and results reviewed by Science Advisory Panel and approved by MDEQ
- Midland Soils RIWP Soil Sampling Work Plan will not be developed until Area Wide Cleanup Criteria has been developed and approved by MDEQ in accordance with Framework for an Agreement
- Midland Soils RIWP Schedule will be developed when Midland Soils RIWP Soil Sampling Work Plan is developed
- Human Health Risk Assessment Work Plan cannot be developed until Notices of Deficiency HHRA responses have been prepared which is due on December 1, 2006. The timing in the schedule is considered a placeholder and will be updated with the December 1, 2006 submittal.
- Feasibility Study, Remedy Evaluation, Remedy Selection, Remedial Design and Remedy Implementation are placeholders. These cannot be reliably estimated until completion of site characterization and human health risk assessment.
- Science Advisory Panel times for reviews of selected study/work plans cannot reliably estimated at this time. The time will vary based upon the complexity of the study/work plan they are being requested to review and provide comment.

ATTACHMENT C

Conceptual Human Exposure Models

In accordance with Section 20120a(3), conceptual human exposure models (CHEM) were developed for each of the two human health risk assessments (HHRA). The CHEMs facilitate identification of the reasonable and relevant human exposure pathways associated with each applicable land use category considering current and foreseeable future land uses. The CHEMs for the Midland Area Soils are presented in Figures 1, 2, and 3 and for the Tittabawassee River and Floodplain Soils in Figures 4, 5, and 6. These figures were developed in the context of the Michigan Department of Environmental Quality's (MDEQ) Part 201 land use category regulatory structure. The applicable land uses include residential, commercial, industrial, agricultural, and recreational land uses for both the Midland Area Soils and the Tittabawassee River and Floodplain Soils (TRFP) Study Areas.

The current exposure pathways identified in the CHEMs are based on potential exposures resulting from soil that has been potentially affected by polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs). The CHEMs may be modified depending on the PCOIs ultimately included in the risk assessment. A rationale for designating an exposure pathway as relevant but not significant will be provided before proceeding to the quantitative PRA.

The human exposure pathways have been identified by evaluating the various ways in which a potential constituent of interest (PCOI) could move from the affected environmental medium (*i.e.*, soil) to a receptor, and then taken into the body through ingestion, inhalation, or dermal exposure. All potentially exposed human receptor populations were identified for each applicable land use category to ensure that the media and exposure pathways that pose the greatest potential

human health risk are identified and evaluated in the probabilistic risk assessment (PRA)

The exposure algorithms used to assess potential health risks for all relevant and significant exposure pathways are presented in the Human Health Risk Assessment (HHRA) work plans. Information on contact rates for specific exposure media will be developed and used to generate exposure distributions for use in the PRA.

Residential ; Commercial I ; and Agricultural Land Uses

Figures 1 and 4 illustrate the human exposure pathways associated with potential exposures to PCOIs in the Midland and TRFP Study Area Soils under a residential land use scenario, respectively. These pathways and the approach to evaluate potential health risk to the identified receptor populations are described in detail below.

Contact with Soil and Dust

Current and future residents in the Midland and TRFP Study Areas might be exposed to PCOIs through incidental contact with soil and dust on their property. This contact may include incidental ingestion, dermal absorption, and inhalation of airborne dust. Contact rates (ingestion, dermal, and inhalation) for adults and children vary and will be accounted for in the exposure assessment. The assumptions used to estimate these exposures will incorporate probabilistic distributions to address the full range of potential contact rates. Actual house-dust data and/or information from the on-going University of Michigan Dioxin Exposure Study (UMDES) and the Michigan Department of Community Health (MDCH) Preliminary Exposure Investigation (PEI) may be used or acquired to

reduce uncertainty concerning potential exposure to PCOIs from house dust. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors will be considered to more accurately characterize potential exposure.

Ingestion of Midland and TRFP Locally Grown Vegetables and Fruits

Current and future residents in the Midland and TRFP Study Areas may grow their own vegetables and fruits and, therefore, may potentially ingest PCOIs by ingesting produce from gardens. An age-adjusted approach to account for differential consumption rates of vegetable and fruits between children and adults is appropriate for this pathway based on information presented in USEPA guidance and other sources. Information on consumption rates for locally grown produce as a subset of total produce consumption will be used to generate the exposure distributions for these variables for use in the PRA. Models of plant uptake of PCOIs will be evaluated and a site-specific study of vegetable uptake is being considered.

Ingestion of Locally Raised Meat, Dairy, and Eggs

This pathway is potentially relevant for residents at agriculturally zoned properties located in the TRFP. Estimates of consumption rates for locally raised meat, dairy and eggs will be used to generate the exposure distributions for this variable. Additional studies to generate site-specific data for this pathway are being considered. Potential risks attributable to ingestion of meat, dairy and eggs raised in the TRFP as a subset of total ingestion rates for these foods will be assessed using site-specific data.

Exposures from this pathway are not applicable to Midland residents because local ordinances prohibit raising agricultural animals in the City of Midland.

Ingestion of Locally Caught Fish and Game

Current and future residents in the Midland and TRFP Study Areas may ingest PCOIs from eating fish and game harvested from the TRFP Study Area. Potential risks attributable to ingestion of fish and game harvested in the TRFP as a subset of total meat and fish ingestion will be assessed using site-specific data.

Contact with Surface Water and Sediment

Current and future residents in the Midland and TRFP Study Areas may incidentally contact PCOIs through contact with surface waters and sediments associated with the Tittabawassee River during activities such as swimming and wading. Contact (incidental ingestion and dermal absorption) with surface waters and sediments will be assessed for both Study Areas. Site-specific information on concentrations of sediment in water, and concentrations of PCOIs in sediment will be used to generate the exposure distributions for use in the PRA. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors may be needed to more accurately characterize potential exposure.

Commercial II, III and IV and Industrial Land Uses

Figures 2 and 5 illustrate the relevant human exposure pathways for land uses that have zoning designations consistent with the Part 201 Commercial II, III, IV, and Industrial categorizations. These pathways and the approaches for evaluating potential health risk to the identified receptor populations are described in detail below.

Contact with Soils and Dust

Current and future workers in the Midland and TRFP Study Areas may come into contact with PCOIs through incidental contact with soil and dust while at work. This contact may include incidental ingestion, dermal absorption, and inhalation of airborne dust generated by various outdoor activities performed at the work property, such as mowing lawns, agricultural activities, and vehicular traffic. Exposures for this pathway will be characterized for adults for each of these land uses. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors will be considered to more accurately characterize potential exposure. The assumptions used to estimate these exposures will incorporate probabilistic distributions to address the full range of potential contact rates.

Ingestion of Locally Grown Vegetables, Fruits, Dairy, Eggs, and Meat

Current and future workers in the Midland and TRFP Study Areas may purchase or obtain these categories of foods locally produced within the Midland and TRFP Study Areas. Although this exposure pathway is potentially relevant, the exposure is not derived from soil at the worker property, and is not directly applicable to workers. Information on consumption rates for locally-grown produce as a subset of total produce consumption will be used to generate the exposure distributions for these variables for use in the PRA.

Contact with Surface Waters and Sediments

Current and future workers in the Midland and TRFP Study Areas may incidentally contact PCOIs through contact with surface waters and sediments associated with the Tittabawassee River in the course of occupational activities.

Contact (ingestion and dermal absorption) with surface waters and sediments will be assessed for both Study Areas. Site-specific information on concentrations of sediment in water, and concentrations of PCOIs in sediment will be used to generate the exposure distributions used to characterize this pathway for the PRA. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors will be considered to more accurately characterize potential exposure.

Recreational Land Use

Figures 3 and 6 illustrate the relevant potential exposure pathways for Midland soils and the TRFP under a recreational land use scenario. Potential receptor populations may include, but are not limited to, hikers, bikers, water-sport enthusiasts, student athletes, out-of-area sportspersons, and other recreational users. These pathways and the approach to evaluate potential health risks to the identified receptor populations are described below.

Contact with Soils and Dust

Current and future persons in the Midland and TRFP Study Areas may come into contact with PCOIs at recreationally zoned properties through incidental contact (ingestion, dermal absorption, and inhalation) with soil and dust while engaging in various recreational activities at these properties. Receptor populations will include children and adults. Contact rates for adults and children vary and will be accounted for in the exposure assessment. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors will be considered to more accurately characterize potential exposure. The assumptions used to estimate these exposures will incorporate probabilistic distributions to address the full range of potential contact rates.

Ingestion of Wild Game and Fish

Current and future persons in the Midland and TRFP Study Areas may ingest certain PCOIs from fish and game harvested from the Tittabawassee River or floodplain. Potential risks attributable to ingestion of fish and game harvested in the TRFP as a subset of total meat and fish ingestion will be assessed using site-specific data.

Contact with Surface Water and Sediment

Current and future recreational users of the TRFP Study Area may incidentally contact PCOIs through contact with surface waters and sediments associated with the Tittabawassee River following recreational activities. Contact (ingestion and dermal absorption) with surface waters and sediments will be assessed in the TRFP Study Area. Site-specific information on concentrations of sediment in water, and concentrations of PCOIs in sediment will be used to generate the exposure distributions used to characterize this pathway for the PRA. Additional site-specific data inputs concerning behavioral, activity-related, and climatic factors will be considered to more accurately characterize potential exposure.

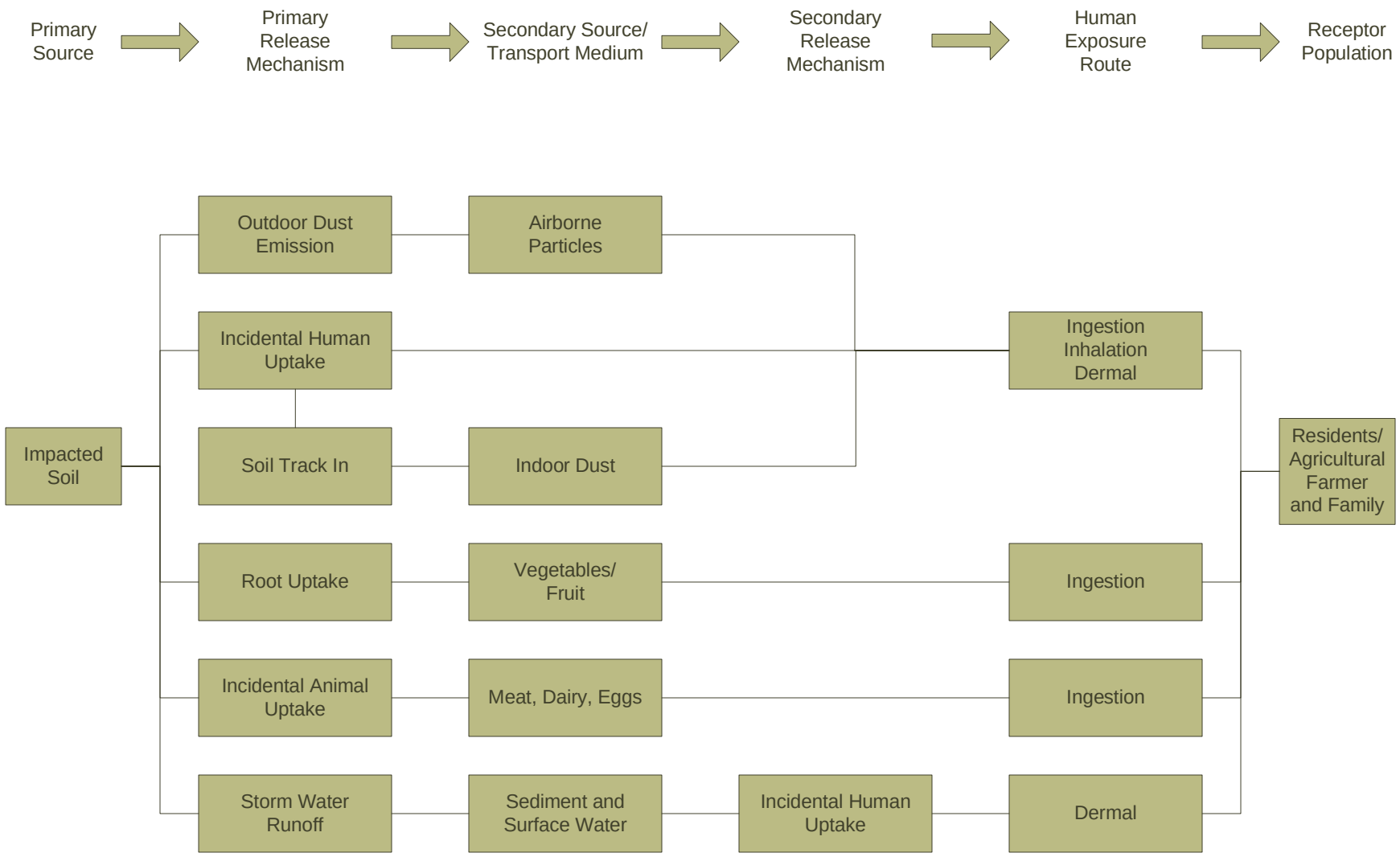


Figure 1. Midland Area Soils Conceptual Human Exposure Model for Residential and Agricultural Land Uses

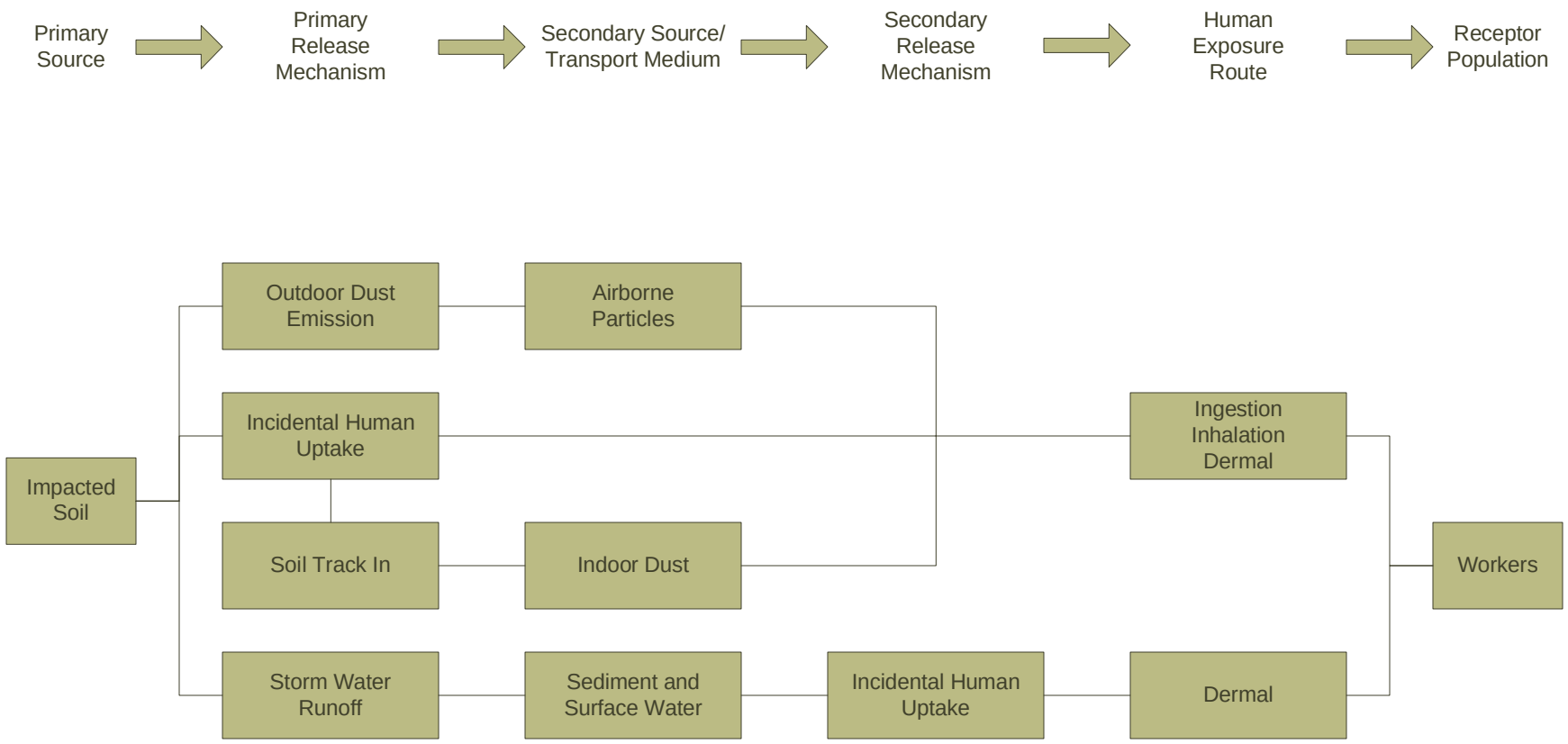


Figure 2. Midland Area Soils Conceptual Human Exposure Model for Industrial and Commercial Land Use

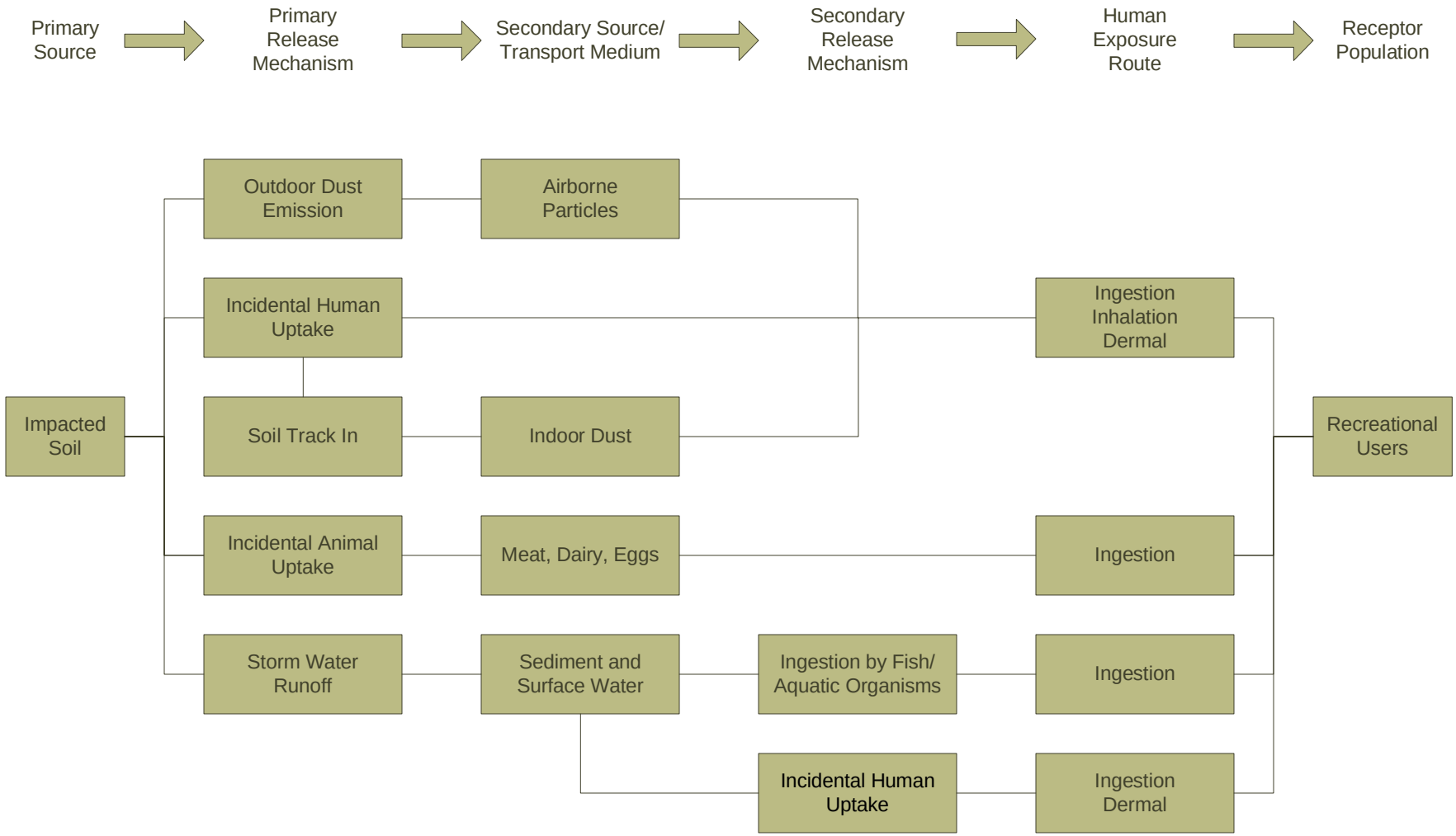


Figure 3. Midland Area Soils Conceptual Human Exposure Model for Recreational Land Use

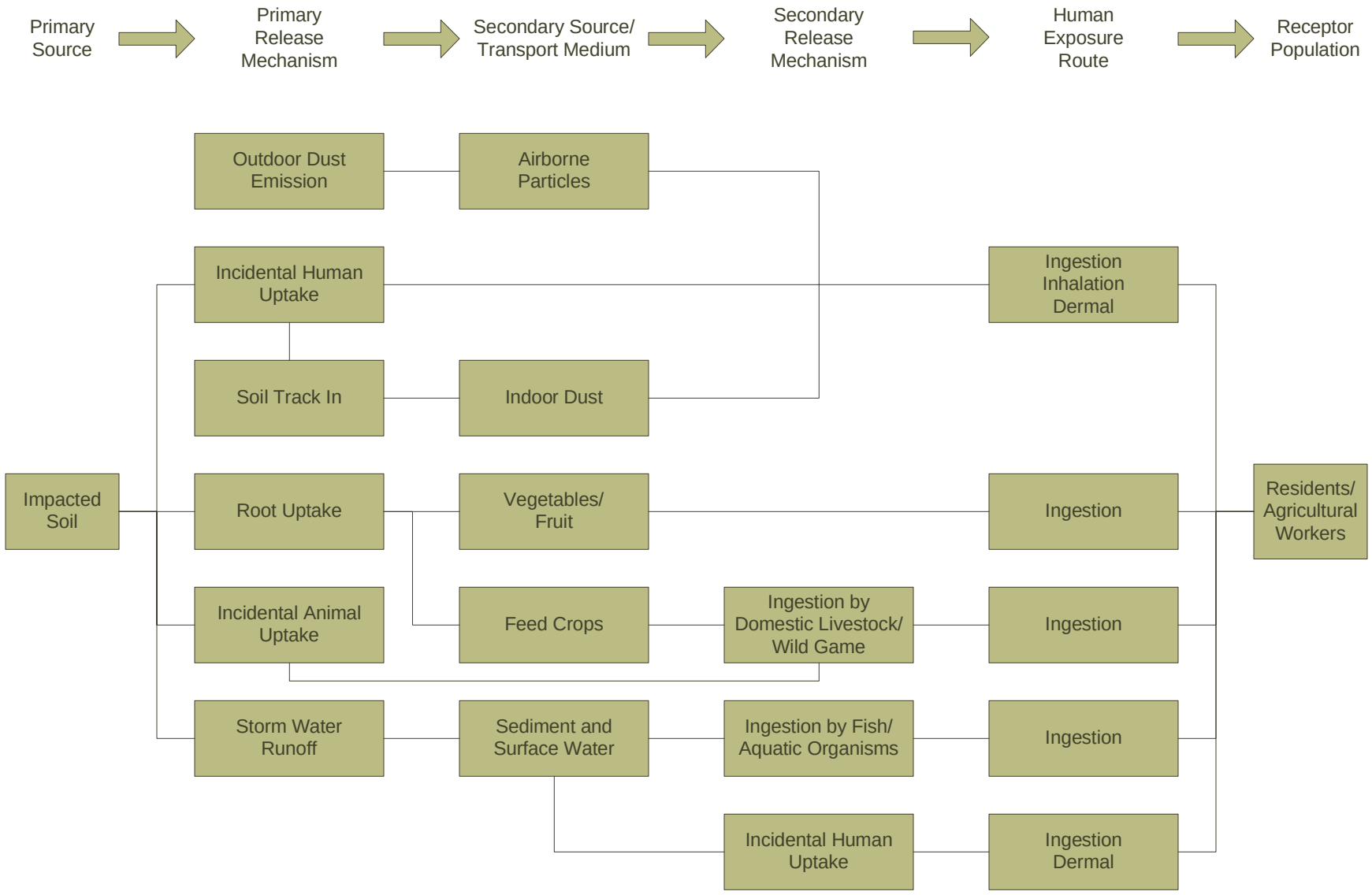


Figure 4. Tittabawassee River Floodplain Conceptual Human Exposure Model for Residential and Agricultural Land Uses

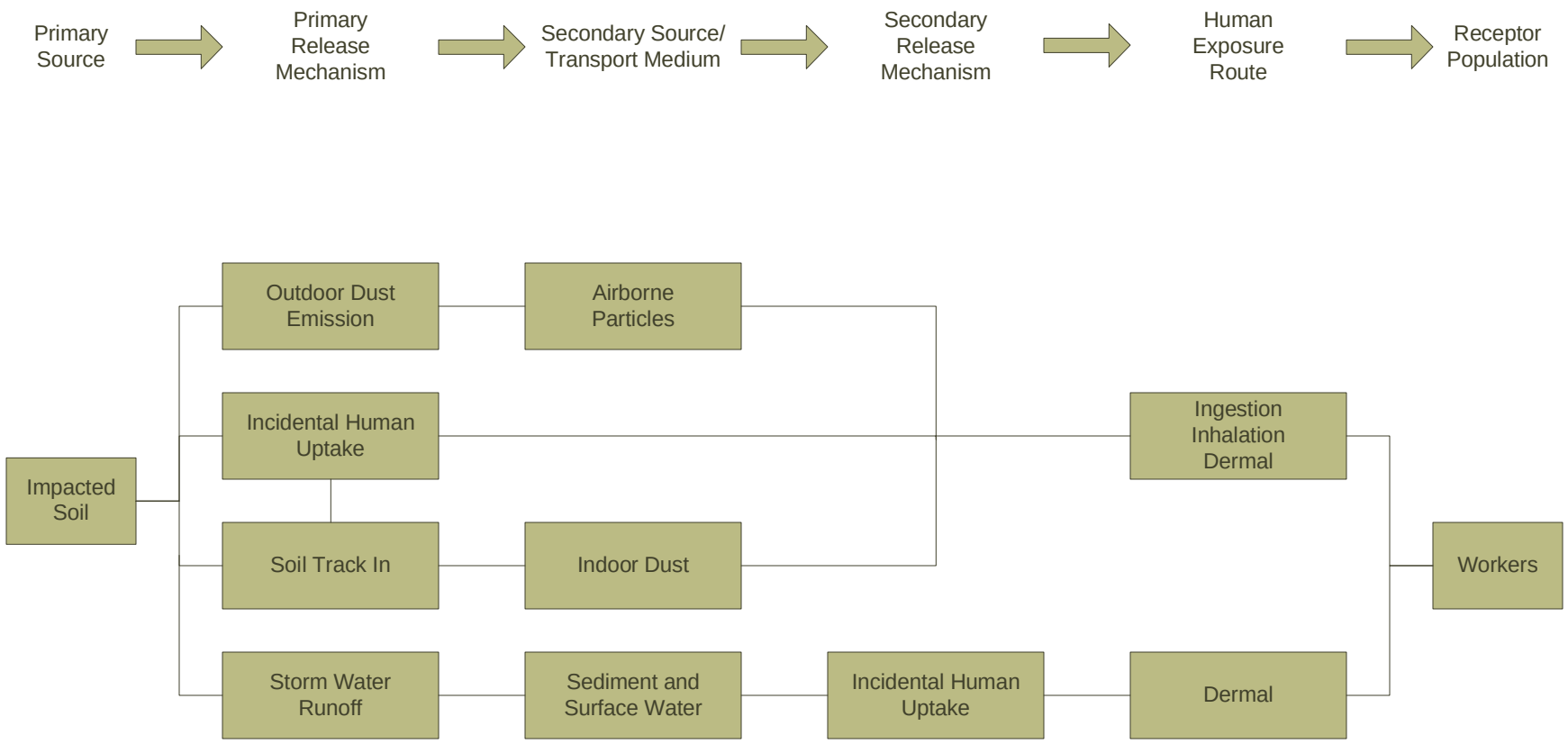


Figure 5. Tittabawassee River Floodplain Conceptual Human Exposure Model for Industrial and Commercial Land Uses

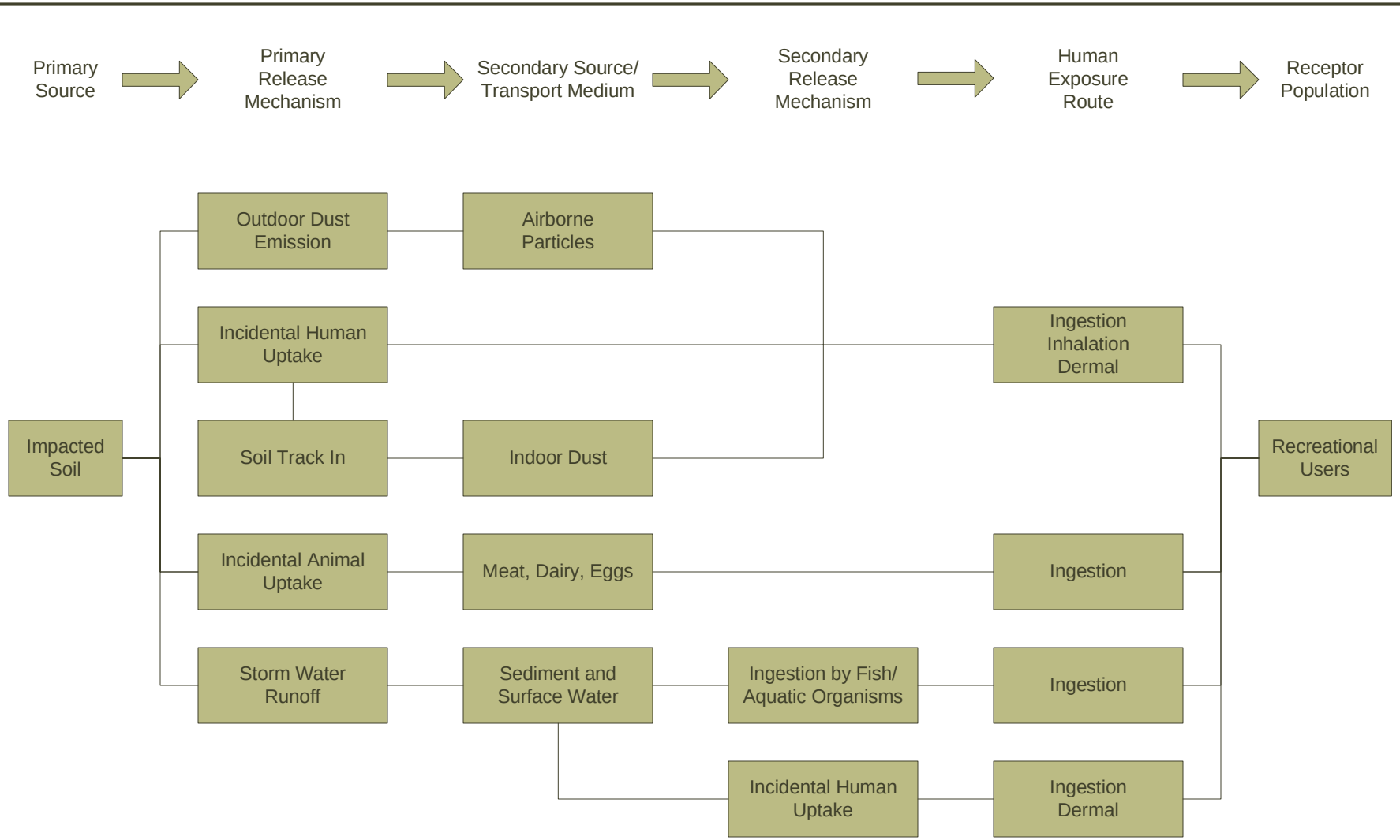


Figure 6. Tittabawassee River Floodplain Conceptual Human Exposure Model for Recreational Land Use

ATTACHMENT D

TECHNICAL MEMORANDUM

PCOI IDENTIFICATION AND DEVELOPMENT OF TARGET ANALYTE LIST

Introduction

In response to the April 13, 2006 Notice of Deficiency issued by the Michigan Department of Environmental Quality to The Dow Chemical Company (Dow), this technical memorandum describes the development of the Target Analyte List (TAL) for the City of Midland and the Tittabawassee River and its floodplain. This memo describes how the Initial Analyte List (IAL) was narrowed down to a list of the Potential Contaminants of Interest (PCOI) and further reduced to the TAL as presented in Table 4-3 (Target Analyte List from Tittabawassee River and Floodplain Remedial Investigation Work Plan, December 2005). The objective of this list is to identify any relevant substances that should be considered for testing under future sampling work.

As of May 1, 2006, Dow has made a good faith effort to identify raw materials, products, by-products, and waste streams used or generated over the more than 100 years of production at the Midland facility and to evaluate its materials handling and waste management practices.

Dow has produced over 1,000 inorganic and organic products since the facility's inception in 1897. The Company and industry practices and requirements for the collection of information and retention of documents for raw material and waste profiles, range from non-existent to very detailed, with the more detailed information generally being available for currently and recently manufactured products and waste streams. For many of the historic products, there may have been limited records maintained on raw materials and possibly little, if any, information collected on waste streams, as there were no regulatory requirements in existence. As such, Dow is unable to represent that available records and other information provide an inclusive depiction of all production and waste management practices over the entire operating life of the facility.

Nonetheless, informative records do exist, and Dow has made a reasonable, good faith effort to discern what those records indicate in the way of chemicals used and produced, and wastes generated and managed, by the facility over time. Consequently, this information provides a sound basis for Dow to compile an Initial Analyte List (IAL), develop from that a Potential Contaminants of Interest (PCOI) list which is narrowed down to a Target Analyte List (TAL).

Methodology for TAL Selection

The methodology summarized below for the selection of the TAL is applicable to both Midland and the Tittabawassee Rivers.

Step 1: Initial Analyte List (IAL) Development and Potential Contaminants of Interest (PCOI) Identification

The methodology for the selection of the IAL submitted to MDEQ in December 2005 (Table 4-2, Initial Analyte List and Chemical Properties from Tittabawassee River and Floodplain Remedial Investigation Work Plan, December 2005) was implemented in several stages using various sources of information. Initially, a list of constituents was identified from the following sources:

- Resource Conservation and Recovery Act (RCRA) groundwater monitoring constituents (Appendix IX, 40 Code of Federal Regulations, Chapter I, Part 264)
- Chemicals monitored under the Midland Plant's National Pollution Discharge Elimination System (NPDES) permit
- Chemicals monitored under the Midland Plant's Revetment Groundwater Interception System (RGIS) groundwater monitoring program
- Chemicals measured in fish tissue as part of caged fish studies in the Tittabawassee River (Woodburn, et al., 2003; MDEQ, 1996).

From these sources, the IAL presented in Table 4-2 (see reference above) included chlorinated benzenes, chlorinated ethers, chlorinated pesticides, chlorinated phenols, dioxins and furans, herbicides, high-molecular-weight PAHs, low-molecular-weight PAHs, metals, nitrobenzenes, nitrosamines, organic nitrogen compounds, PCBs, phenolic compounds, phthlates, SVOCs, and VOCs. From this list of substances, a list of Potential Contaminants of Interest (PCOI) was generated to account for the types of chemicals that may have been released from the Midland Plant and may be present in the study area media.

Step 2 highlights how the IAL and PCOI were narrowed down to the TAL after a careful review of each constituent's environmental fate.

Step 2: Target Analyte List (TAL) Development

Chemical compounds on the PCOI list were evaluated according to several criteria including those found in the *Persistent, Bioaccumulative and Toxic (PBT) Profiler*. The PBT Profiler is a screening-tool designed to estimate the overall environmental persistence of chemical compounds based on the following criteria:

- Physical and chemical properties
- Half-life
- Vapor pressure
- Bio-concentration factors
- Photo-degradation rates
- Bio-degradation rates

Additional criteria, including process knowledge and method of contaminant distribution, were also considered. Certain manufacturing processes, by-products and potential contaminants were also evaluated according to process knowledge. The method of contaminant distribution was a factor since the fate of compounds is different for aqueous discharges (Tittabawassee River) in comparison to airborne distribution (City of Midland). Aqueous discharge was the primary source of distribution of contaminants into the Tittabawassee River. Over the years, the number of outfalls for Michigan Operations has been reduced from 11 down to one primary process wastewater discharge location with two emergency backup outfalls and several stormwater outfalls. Since, airborne emissions were the primary source of contaminant deposition in the City of Midland, the fate of compounds to be considered is different for the Midland RIWP.

The chemical's persistence in the environment was established, ranging from not persistent to very persistent. Chemicals that are not volatile, i.e. $F_v < .99$, and that are persistent in soil were retained from the PCOI list as target analytes. Some of the analytes from the Caged Fish studies lists were not retained on the PCOI list because they were found to be non-persistent. Chemicals that tend to volatilize and that are not persistent in soil were not carried through to the TAL.

The TAL was narrowed down to include chlorinated pesticides, dioxins and furans, herbicides, high-molecular-weight PAHs, metals, PCBs, phthlates and SVOCs (Table 4-3, Target Analyte List from Tittabawassee River and Floodplain Remedial Investigation Work Plan, December 2005).

Additional Review of TAL

Dow Additional Review

Since January 2006, a historical review was conducted of Dow Midland manufacturing operations. Sources for this review were compiled from historical documentation at the Post Street Archives in Midland, Michigan. From this historical documentation, a list of chemicals produced since the site's inception in 1897 was composed. Using this list, an additional evaluation of the TAL presented in the December 2005 RIWP submission for the Tittabawassee River will be completed to determine if the TAL is appropriately inclusive of chemicals. This will include further record searching and chemical evaluations of raw materials, products, wastes, and by-products using the methodologies described above. Furthermore, other compounds such as certain chlorinated and brominated isomers of biphenyls, biphenylenes, napthalenes, diphenyl ethers, dibenzothiophenes, and azo/azoxy benzenes will also be considered for inclusion on the TAL. Based on this review, the additional evaluation for the Tittabawassee River RIWP TAL will be completed and submitted to the MDEQ by June 1, 2006. During this review, efforts will be made to establish time periods for releases of certain substances or groups of substances in order to assist the GeoMorph work. The TAL for the focused sampling plans (i.e., fish tissue, farmer dust, etc.) is specified in each of those plans. The previous proposal to eliminate from further consideration substances which are not detected in more than 5 percent of sample analytical results is revised to eliminate the 5 percent provision. Substances will be eliminated from further consideration on a substances specific basis after considering numerous factors such as location of detections, concentrations found, and frequency of detections.

MDEQ Potential Sampling

The Midland RIWP submitted in December 2005 contains the TAL which will remain as the TAL for that work plan, but that TAL may be expanded in the event MDEQ performs additional sampling within the Michigan Operations plant boundary. Additional constituents from that MDEQ sampling will be added to the Midland TAL if the data are received by Dow from the MDEQ before the sampling and analyses have been initiated under the Support Study, and after discussions with the MDEQ to determine if the concentrations found, location of detections, relative toxicity of the substances found, frequency of detections and analytical certainty of the detection would warrant inclusion on the TAL. Samples taken in proximity (the first two sample stations along each transect regardless of the current land use) to the Dow Midland Plant will be analyzed for an expanded TAL.

References

Tittabawassee River and Floodplain Remedial Investigation Work Plan, CH2MHill, December 2005.

Midland Area Soils Remedial Investigation Work Plan, CH2MHill, December 2005

PBT Profiler. 2005. Persistent, Bioaccumulative, and Toxic Profiles Estimated for Organic Chemicals On-Line. Accessed December 1, 2005. http://www.pbtprofiler.net

Attachment E

Activity Survey Study Plan

Activity Survey Study Plan

Study Objectives

1. Develop survey instruments (questionnaires and diaries) that elicit information about normal variations in site-specific activities that bring humans into potential contact with local contaminated environmental media (*e.g*., soil, sediment, dust, fish, native game, local livestock, eggs, milk and garden crops, and so forth). The endpoints measured will be specifically designed to match and replace the exposure inputs for the various site-specific exposure pathways relevant to the Human Health Risk Assessment (HHRA).
2. Develop the questionnaire format in such a way that allows the information to be extracted and developed for quantitative use in the HHRA exposure assessments.
3. Identify and recruit area residents to participate in a retrospective questionnaire-based survey on lifestyle and behavioral factors relevant to exposure estimates.
4. Identify and recruit a subset of those residents to further participate in a prospective diary study that provides additional information on the lifestyle and behavioral issues relevant to exposure issues.
5. Identify specific populations with unique exposures and determine their interactions with the study area.
6. Ensure the information gathered from the surveys is quantified in such a way as to be able to evaluate site- or activity-specific exposures for various land uses and exposures.
7. Assure that the data collected are sufficient in terms of quality and quantity to evaluate the variability distributions needed for a site-specific HHRA.

1.0 Introduction

All risk assessments utilize a number of assumptions regarding human behavior that impact the magnitude of exposure estimates for a variety of exposure pathways. These include assumptions on contact rates, and frequency and duration of various activities that bring humans into contact with contaminated media of one type or another. Many of the standard assumptions have been developed over the years from data collected in different geographical areas among different populations. Often the study or studies that furnish the underlying exposure information used to create the assumption have only a small number of individuals involved, occur over a limited time, or in an area which differs from the area under consideration in a number of ways (*e.g.*, meteorological, socioeconomic, racial or ethnic). In other cases, these studies may be somewhat dated or have technical flaws that limit how applicable they are to a specific risk assessment. One goal of the risk assessment process is to reduce uncertainty by developing data specific to the issue at hand. Accordingly, it is desirable to augment standard assumptions by collecting and using site-specific, quantitative exposure information in the Human Health Risk Assessment (HHRA). Such information will be combined with other aspects of the exposures identified to evaluate site-specific variability distributions for use in the exposure assessment portion of HHRA.

In addition, activity and behavioral data obtained in the University of Michigan Dioxin Exposure Study (UMDES) will be evaluated for use in the HHRA including combining the UMDES data with activities and behavioral data gathered in the HHRA-specific Activities Survey. Plans are currently underway to determine how data and data analyses from the UMDES can be used in developing the HHRA exposure PDFs. This potential use of the UMDES data will be better understood when the UMDES results are officially released and available in August of 2006.

2.0 Population Surveyed

The primary population of interest consists of residents of Midland, Michigan and those living downstream of Midland along the Tittabawassee River. Exposures of potential concern have been identified in discussions with the Michigan Departments of Environmental Quality (MDEQ), Community Health (MDCH), and Agriculture (MDA). These discussions serve as the basis for the populations and activities to be studied in the Activity Survey. It is planned to try to recruit approximately 500 to 1000 households to participate in the retrospective questionnaire-based portion of the Activity Survey. Half of these will be drawn from the population of Midland and the remaining half from the rural population downstream of Midland. A subset of 100 to 250 households will be recruited to participate in the prospective diary portion of the survey.

Questions about populations with possibly unique exposures, such as Native Americans, have also been raised by the State and tribal representatives, and will also be addressed in the survey. In this instance, an initial meeting will be held with tribal representatives to determine which activities are unique to this population and where they occur. Those activities determined to occur in contaminated areas and which have the potential to cause exposures different from the larger resident populations will be developed into a survey module and administered to a subset of this population.

3.0 Participant Selection

Recruitment for the Activity Survey will be conducted through random digit dialing or another selection technique designed to generate a random selection of participants. The recruitment will be preceded by local mailings and press releases to alert the public and that explain the survey, the information solicited, and its intended use. The actual survey will be conducted in a face-to-face interview and is anticipated to require no more than 90 minutes to complete. The survey will be administered over at least two (*i.e.*, summer and winter), and perhaps all four, seasons in order to gather behavioral or activity information that may change according to the season. It will be made clear that identities of participants will remain confidential (all forms will be coded with names associated with those codes held separately and only used for re-contact for purposes of this survey), no information from individual households or persons will be identified, and that data collected will be used in the aggregate to develop exposure variables unique to the area or populations surveyed.

While priority will be given to recruiting participants along the Tittabawassee River and from areas of the Midland thought to be impacted by contaminants, the primary focus of the Activity Survey is to collect behavioral information that is unlikely to vary significantly throughout the area or between populations. Therefore, the goal of this effort will remain focused on collecting useful exposure data common to local residents as opposed to selecting only residents who may live in affected areas.

If any unique activities potentially resulting in exposure are identified among Native Americans that use the affected areas, these activities will be incorporated as an additional module for the Activity Survey, and added to the overall Activity Survey. If tribal representatives agree, the population-specific questions will be reviewed by tribal representatives for clarity, relevance, and accuracy, and then administered to a subset of the local tribal population who agree to participate. The survey will be introduced through a letter from the tribal authorities to the tribal members with a request for cooperation, if contacted. Tribal members will be selected randomly from the list of tribal members resident in the area. These households will be contacted by phone or otherwise, and asked to participate on the same terms as the other participants. A subset of this group may also be asked to participate in the prospective diary portion of the study.

4.0 Survey Management

Administration of a large and complicated Survey requires a significant commitment of resources and prior experience is necessary to a successful effort. This Study plans to retain a University-based Survey Research Laboratory (SRL) or a Professional Survey Research Organization (PSRO) to manage the logistics of the Survey, assist in the development and administration of the questionnaire and diary, and develop the database containing the responses as well as provide input on data analyses. The SRL or PSRO selected will be independent and have had prior experience with administration and interpretation of complex surveys. Special preference will be given to those organizations that are located in the Mid-West and have had specific experience with environmental issues.

5.0 Pilot Testing

The questionnaire will be developed in conjunction with the State and tribal representatives. The SRL or PSRO will be available to meet with the stakeholders at this stage to assist in the development of and pilot test the questionnaire and diary.

Once the survey instruments are drafted, the SRL or PSRO will pilot test to determine the length of time required to complete, identify logistical needs, and assess any difficulties in interpreting the questions or carrying out the survey. The pilot test will be carried out in a population outside the Midland/Saginaw/Tittabawassee River area, but in an identical manner to that intended for the actual surveys. Any revisions to questions, format, or administration required will be documented and the questionnaire and diary re-tested in naïve populations until the questionnaire and diary are finalized.

6.0 Survey Administration

The SRL or PSRO will identify and recruit experienced survey takers who are acquainted with the questionnaire-based surveys and diaries, and are trained in this specific questionnaire and diary to administer the Activity Survey. A work plan for the logistics, a training manual for surveyors, and field guide will be developed by the SRL or PSRO to address the proper administration of the questionnaire and diary and identify potential problems and their solutions. The surveys will be administered personally to each head of a participating household, and it will be administered at least twice to the same household, once in the winter and summer, and possibly in all four seasons if responses appear to vary significantly.

The diary portion of the survey will consist of a subset of the households that volunteer to participate in the questionnaire survey. Each adult member (age 16 and over) of the household will be asked to complete an activity diary that details their behavior in 30-minute increments over one to two weeks. An adult member of the household will be asked to record the behavior of the minor children in household. The diary will be constructed to elicit specific responses regarding behaviors likely to result in exposure to contaminated environmental media. Again, a diary will be kept for at least two and possibly all four seasons by study participants. Survey collectors will call the participants during these periods to make sure the diaries are being completed and answer any questions.

7.0 Survey Audit

A minimum of 10% of the questionnaires administered will be audited by survey team leaders to ensure that the questionnaires were completed by the named individual and completed correctly. If inconsistencies are found, additional questionnaires completed by that surveyor or survey team would be audited. Any problematic questionnaire(s) would be re-administered or discarded if they cannot be re-administered.

The diaries will also be audited at a similar rate to see if they appear to have been completed accurately and fully. Any information from a diary that is viewed as questionable will be discarded.

8.0 Survey Instrument

The Activity Survey will be conducted in two phases as noted. The first phase will take the form of a retrospective questionnaire administered to a cross-section of the Midland and Tittabawassee River populations. The questionnaire will be developed using standard questionnaire software to aid its design and with closed-end questions to limit response variability. Questionnaires have been used successfully to furnish exposure and use information for epidemiology and risk assessment (Ahlborg, 1990; Gerin, 1990; Miligi and Masala, 1991; Joffe, 1992; Pollock *et al.*, 1994; Blatter *et al.*, 1997). In most cases, face-to-face interviews are more successful than mail, telephone or web-based

surveys. The questionnaire will be developed in modular form to cover multiple activities that bring adults and children into direct contact with contaminated media and be designed such that these activities can be quantified in terms of duration, frequency, and amount. The questionnaire will be administered in a face-to face setting with the self-designated head of the participating household and will take approximately 90 minutes. Because certain behaviors of interest may change over the year due to weather (*e.g*., soil contact during winter) or seasonal issues (*e.g.*, hunting or fishing seasons), the questionnaire, or portions of it, will be administered at least twice during the year (winter and summer) and perhaps all four seasons. If necessary, an additional module of questions specific to unique activities associated with the Native American population will be developed as noted above and used to develop an understanding and quantitative estimate of such exposures among this population

An example of a question series that might be employed to explore fish ingestion follows:

1) Do you or any member of the household fish in the Tittabawassee River?
   a) Yes (go to Question #2)
   b) No (skip to Question #X)
   c) I don't know

2) How often do you or any member of the household fish in the Tittabawassee River?
   a) Daily
   b) 2-3 times a week
   c) Weekly
   d) 2-3 times a month
   e) Monthly
   f) 2-3 times a year
   g) Once a year
   h) Less than once a year
   i) We don't fish in the Tittabawassee River
   j) I don't know

3) When you or any member of the household fish in the Tittabawassee River, what fish do you primarily catch?
   a) Walleye
   b) Northern Pike
   c) Smallmouth Bass
   d) White Bass
   e) Channel Catfish
   f) Carp
   g) Other Species_____
   h) I don't know

4) What is the second fish species that you or a member of your household most commonly catch from the Tittabawassee River?
   a) Walleye
   b) Northern Pike
   c) Smallmouth Bass
   d) White Bass
   e) Channel Catfish
   f) Carp
   g) Other Species_____
   h) I don't know

5) What is the third fish species that you or a member of your household most commonly catch from the Tittabawassee River?
   a) Walleye

b) Northern Pike
c) Smallmouth Bass
d) White Bass
e) Channel Catfish
f) Carp
g) Other Species_____
h) I don't know

6) In the last month, how many times did you or your family go fishing in the Tittabawassee River?

a) more than 10
b) 8 to 9
c) 6 to 7
d) 4 to 5
e) 2 to 3
f) once
g) Did not fish in the last month

7) What type of fish did you catch most and how many and how much did you catch (number and nearest total pounds).

a) Walleye_____
b) Northern Pike_____
c) Smallmouth Bass_____
d) White Bass_____
e) Channel Catfish_____
f) Carp_____
g) Other Species_____
h) I don't know
i) No Catch or Catch and Release

8) Do you eat your catch from the Tittabawassee River?

a) Yes
b) No (Skip to Question #X)
c) I don't know

9) What Tittabawassee River fish do you and your household eat the most? *(question repeated for second and third most commonly consumed fish)*

a) Walleye
b) Northern Pike
c) Smallmouth Bass
d) White Bass
e) Channel Catfish
f) Carp
g) Other Species_____
h) We don't eat river fish
i) I don't know

10) For this species of Tittabawassee River fish, how do you prepare your catch? *(refer to chart; question repeated for second and third most commonly consumed fish)*

a) Filet – skin on, untrimmed
b) Filet – skin on, trimmed
c) Filet – skin off, untrimmed
d) Filet – skin off, trimmed
e) Whole Fish – skin on
f) Whole Fish – skin off
g) I don't know

11) How many times in the past month did you and your household eat this species of Tittabawassee River fish? *(question repeated for second and third most commonly consumed fish)*

a) More than once a day
b) Once a day
c) 3-5 times a week
d) 1-2 times a week

e) 3-5 times a month
f) 1-2 times a month
g) Once a month
h) We did not eat any Tittabawassee River fish last month

12) How do you mostly cook this species of fish? *(question repeated for second and third most commonly consumed fish)*

a) Grilled
b) Broiled
c) Barbequed
d) Pan-fried
e) Deep-fried
f) Stewed
g) Other_____
h) I don't know

13) When you eat a meal of the household's preferred Tittabawassee River fish, how much do you eat at a sitting? *(refer to meal size chart; question repeated for second and third most commonly consumed fish and different family members)*

a) Less than one filet (less than 4 ounces)
b) 1-2 filets (1/4 to 1/2 pound)
c) 3-4 filets (3/4 to 1 pound)
d) 5-6 filets (1-1/4 to 1-1/2 pounds)
e) 7-8 filets (1-3/4 to 2 pounds)
f) 9-10 filets (2-1/4 to 2-1/2 pounds)
g) 11-12 filets (2-3/4 to 3 pounds)
h) More than 12 filets (more than 3 pounds)
i) I don't know

The final set of nested, closed-ended questions for each module will be developed in conjunction with MDEQ and other stakeholders in consultation with the SRL or PSRO. The format and responses will be pilot-tested to ensure compatibility with the Study goals and objectives and the reliability and usability of the information elicited from participants.

The second phase of the Activity Survey consists of a prospective exposure diary kept by a subset of the above populations to validate the results of questionnaire. The diary will divide the day into 30-minute increments and all adult members of a participating household will be asked to complete the diary each day for a period of two weeks. An adult member of the household will be requested to fill out a diary for the minor children in the household. The household will be instructed in how to complete the diary and the diary will have instructions and a set of questions to complete on each day. As with the questionnaire, a diary will be kept over at least two seasons and possibly all four to address those issues that vary by season. An example of the diary pages that might be used follows:

Day 1 **Page 1**

Midnight to 12:30AM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____

Other_____

12:30AM to 1AM(check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

.
.
.

6AM to 6:30AM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

6:30AM to 7AM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

.
.
.

Noon to 12:30PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

12:30PM to 1PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

.
.
.

6PM to 6:30PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____

Outside away from home_____
Other_____

6:30PM to 7PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

.
.
.

9PM to 9:30PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

9:30PM to 10PM (check one)

Asleep at home_____
Asleep away from home_____
Awake and inside_____
Awake and inside away from home_____
Outside in the yard_____
Outside away from home_____
Other_____

Day 1 **Page 2**

A) In the last 24 hours, how much time did you spend indoors at home? (Nearest 30 minutes)_____

B) In the last 24 hours, how much time did you spend indoors away from home? (Nearest 30 minutes)_____

C) In the last 24 hours, how much time did you spend outdoors at home? (Nearest 30 minutes)_____

D) In the last 24 hours, how much time did you spend outdoors away at home? (Nearest 30 minutes)_____

E) In the last 24 hours, how much time did you spend outdoors at home doing lawn work? (Nearest 30 minutes)_____

F) In the last 24 hours, how much time did you spend outdoors at home gardening? (Nearest 30 minutes)_____

G) In the last 24 hours, how much time did you spend indoors at home digging in the soil? (Nearest 30 minutes)_____

H) In the last 24 hours, how much time did you spend outdoors at home relaxing? (Nearest 30 minutes)_____

I) In the last 24 hours, how much time did you spend fishing in the Tittabawassee River? (Nearest 30 minutes)_____

J) In the last 24 hours, how many and what kind of fish did you catch from the Tittabawassee River? _____

K) In the last 24 hours, how much Tittabawassee fish did you eat (nearest half pound) and how was it prepared? _____

L) In the last 24 hours, how much time did you spend hunting (Nearest 30 minutes)_____

M) In the last 24 hours, did you take any game while hunting and what was it? _____

N) In the last 24 hours, did you eat any game? (What, how much, and how prepared?)_____

O) In the last 24 hours, did you eat any homegrown garden crops? (What, how much, and how prepared?)_____

P) In the last 24 hours, did you eat any home raised meats? (What, how much, and how prepared?)_____

Q) In the last 24 hours, did you eat any home raised eggs? (How much, and how prepared?)_____

R) In the last 24 hours, did you consume any home raised milk? (How much?)_____

As noted, the labor-intensive nature of the diary requires that it be used for only a short time period, but more than once to capture behaviors that occur only occasionally or which change with the season. The actual and final diary format and probe questions will be jointly developed after discussion with MDEQ and other stakeholders and in consultation with the SRL or PSRO. Because of the complexity of this kind of survey and the interest in the development of useful and relevant exposure data, the questionnaire and diary will be developed and pilot-tested by the SRL in conjunction with MDEQ and other interested parties at the tribal, state, and federal levels to ensure the acceptability of the data and exposure information developed from it to all parties.

9.0 Targeted Behaviors

The Activity Survey will elicit information on time spent at home and work by season for different activities by both children and adults. The specific questions associated with the different activities will be designed to elicit the appropriate and specific response in a manner that allows the answers to describe the activity in a quantitative manner for subsequent use in the risk assessment. As previously mentioned, a meeting or meetings with representatives of the Saginaw-Chippewa Tribe will address any unique tribal exposure issues and locations and ensure that such exposures are accurately represented in a module of the Activity Survey, as well as how best to administer the survey to tribal members. The targeted activities and quantifiable behaviors include time spent engaged

in activities that bring individuals into contact with soil or sediment by season; time spent in recreation by season; time spent fishing or hunting along with species and quantities collected, preparation methods, and rate of ingestion; use of homegrown fruits, vegetables, meats, eggs and milk, preparation methods, and rate of ingestion. Other activities or refinements will be introduced during the actual questionnaire/diary development in order to best capture the quantitative aspects of these exposures. The behaviors/activities of interest can be broadly categorized as follows:

A. Soil, Dust, and Sediment Contact
   - Time spent indoors/outdoors by season and location
   - Time spent outdoors – lawn work
   - Time spent outdoors – gardening
   - Time spent outdoors – digging
   - Time spent outdoors – children play/soil contact
   - Time spent outdoors – leisure (adults & children)
   - Time spent away from home – adults & children
   - Time spent in contact with sediment – adults & children

B. Fish Ingestion
   - Consumption of Tittabawassee River fish
   - Type of Tittabawassee River fish caught for consumption
   - Frequency of fishing in the Tittabawassee River
   - Catching success
   - Preparation of catch
   - Cooking methods employed
   - Number of meals of Tittabawassee River fish/unit time
   - Size of meals/species caught

C. Game Ingestion
   - Consumption of local game
   - Type of local game caught for consumption
   - Frequency/location of hunting
   - Hunting success/species
   - Preparation of game/species
   - Cooking methods employed/species
   - Number of meals of game/take/unit time
   - Size of meals/species taken

D. Livestock, Eggs, and Milk Ingestion
   - Consumption of home- or local raised meats, poultry, eggs, and milk
   - Type of homegrown livestock, milk and eggs consumed
   - Frequency of consumption/livestock, milk and eggs
   - Preparation of eggs, milk, or meats
   - Cooking methods employed
   - Number of meals of livestock, milk, or eggs/unit time
   - Size of meals/livestock, milk, or eggs

E. Garden Crop Ingestion
   - Consumption of home-grown garden crops

- Type of fruits and vegetables grown for consumption
- Frequency of consumption/crop
- Preparation of garden crops
- Cooking methods employed
- Number of meals of homegrown fruits and vegetables/unit time
- Size of meals/homegrown fruits and vegetables

F. Specific Cultural Activities that may increase contact with contaminated media and are not previously addressed.

G. Other activities and behaviors that may increase contact with contaminated media and are not previously addressed.

10.0 Data Evaluation and Development

Exposure data from the questionnaires and diaries will be double entered into an accessible database for analysis of the information collected. The information about a specific activity or behavior will be used to develop a quantitative estimate of that activity or behavior from the descriptive statistics for use in the exposure information. For example, the various questions about fish ingestion used in the example provided are intended to lead to specific information about the amount in grams of a specific species (*i.e.*, Walleye, Smallmouth Bass, Channel Catfish, etc.) consumed per unit time *(e.g*., days, weeks, months). The questions regarding soil contact and seasons are likewise intended to better represent the local frequency and duration (for instance, hours or minutes per day) of adult and child behavior that results in direct soil contact. The Activity Survey data and the site-specific exposure variables derived from it will be reviewed by the state, tribal, and federal agencies as well as by an Independent Science Advisory Panel (ISAP) to validate their bases and use.

11.0 References

Ahlborg GA Jr., 1990. Validity of Exposure Data Obtained by Questionnaire: Two Examples from Occupational Reproductive Studies. Scand J Work Health, 16: 284-288.

Pollock KH, Jones CM, and Brown TL, 1994. Angler Survey Methods and Their Applications in Fisheries Management. Special Publications 25. American Fisheries Association, Bethesda, MD.

Blatter BM, Roeleveld N, Zielhuis GA, and Verbeek ALM, 1997. Assessment of Occupational Exposure in a Population Based Case-Control Study: Comparing Postal Questionnaires with Personal Interviews. Occup Environ Med 54: 54-59.

Gerin M, 1990. Recent Approaches to Retrospective Exposure Assessment in Occupational Cancer Epidemiology. Occup Cancer Epidemiol., 120: 39-49.

Joffe, M., 1992. Validity of Exposure Data Derived from a Structured Questionnaire. Am. J. Epidemiol. 135: 564-570.

Miligi L and Masala G, 1991. Methods of Exposure Assessment of Community-Based Studies: Aspects Inherent to the Validation of Questionnaires. Appl Occup Environ Hyg., 6: 502-507

Attachment F

Site Specific Exposure Study Plans

1. **Fish Tissue Study Plan**
2. **Game Tissue Study Plan**
3. **Domestic Livestock Study Plan**
4. **Garden Vegetable Study Plan**
5. **Stationary Airborne Agricultural Dust Study Plan**
6. **Personal Airborne Dust Exposure Study Plan**

Fish Tissue Study Plan

Study Objectives

1. To identify and collect an adequate number of those species and sizes of fish from the Tittabawassee River most commonly caught and consumed,
2. To identify and sample those Tittabawassee River locations, in which the targeted species most likely occur,
3. To identify the appropriate collection times for the targeted species and implement the sampling at that time,
4. To identify and prepare individual edible portions for analysis in the same manner as is commonly done by consumers of Tittabawassee River fish, and
5. To submit those tissue samples to a qualified laboratory for analysis of Target Analytes (TAs) relevant to the Tittabawassee River

Tissue from the fish sampling will be preserved in case additional or confirmatory analysis is required. The analytical results from the fish tissue sampling will be used to estimate the probability density function (PDF) for concentration and used to estimate TA exposure through fish ingestion. The necessary data inputs, methods and decisions used to create this specific PDF will be detailed in the Exposure Assessment Study Plan currently under development. Other aspects of TA exposure through fish ingestion, such as weighting the consumption of specific fish species and sizes, accounting for cooking loss of TAs, and determining the frequency and rate of consumption will also be detailed in the relevant Exposure Assessment Study Plan currently under development for an anticipated December 1, 2006 submission.

The sampling plan and methods for acquiring qualitative and quantitative data on the species, size, location, and seasonal aspects of fish caught for consumption by licensed anglers in the Tittabawassee River will be developed in part from Creel surveys conducted by the Michigan Department of Natural Resources (MDNR) or other sources of information such as the planned site-specific Activity Survey, the University of Michigan Dioxin Exposure Survey (UMDES) questionnaire information, Michigan Department Community Health (MDCH) fishing survey data, or additional, focused Creel surveys to fill relevant data gaps. Experts on fishing in the Tittabawassee River (*i.e.*, MDNR, U.S. Fish and Wildlife Service (USFWS), local fishing and outdoors guides, *etc*.) will also be interviewed to ensure that the fish sampling effort is site-specific and relevant. Any suggested and relevant modifications to this plan in terms of species, sizes, numbers, and preparation methods based on their inputs will be adopted in order to improve the relevance and site-specificity of the fish sampling protocol, thereby further reducing uncertainty. Planning and documentation of the sampling procedures will be done to ensure that collection activities are time and labor-effective and that sample integrity is preserved. It is anticipated that both collection and analysis of fish tissue can be completed within 12 months following approval of this work plan by MDEQ, completion of the Activity Survey, and subject to the actual fishing seasons.

1.0 Introduction

Historically, fish collected from the Tittabawassee River have been shown to contain residual levels of polychlorinated dioxins and furans as well as other persistent chlorinated substances. Consumption advisories for certain species of fish have been issued by the State of Michigan on this basis. Time trend for 2,3,7,8-TCDD concentrations in native Tittabawassee River Walleye and Carp fillets are depicted in **Figures 1** and **2**. The pre-1990 data were generally collected either by The Dow Chemical Company (Dow) working with Michigan Department of Environmental Quality (MDEQ) or MDEQ working with the US Environmental Protection Agency (US EPA). Dow collected the post-1990 data as part of the Michigan state discharge permit.

Fish from the Tittabawassee River are consumed by sport fishermen and others. This constitutes a completed exposure pathway and requires inclusion and evaluation in the Human Health Risk Assessment (HHRA). The existing data are inadequate for risk assessment purposes because of the limited numbers of fish, species, and size classes sampled, differences in fish preparation, congener analyses, and other factors. Therefore, This Study proposes to implement a plan to collect fish tissue samples for analysis based on species and sizes preferentially caught by sport fishermen and others, and prepared for analysis in the manner most common to these groups as revealed by MDNR Creel Surveys as well as a planned site-specific Activity Survey. Interviews with local experts and other sources will supplement this information (US EPA, 2000). This Study Plan details the methods for collecting, preserving, and shipping fish tissue from the Tittabawassee River to a laboratory for analysis of Target Analytes (TAs) in the edible portions of sport-caught fish.

Figure 1. Time Trend Data for 2,3,7,8-TCDD in Native Walleye Fillet Tissue Taken Downstream of the Dow Dam, 1985 to 2002.

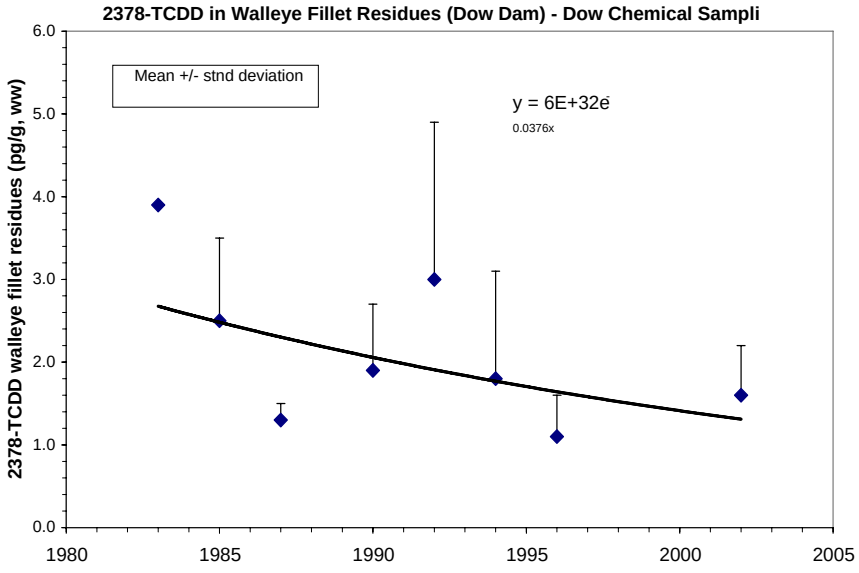
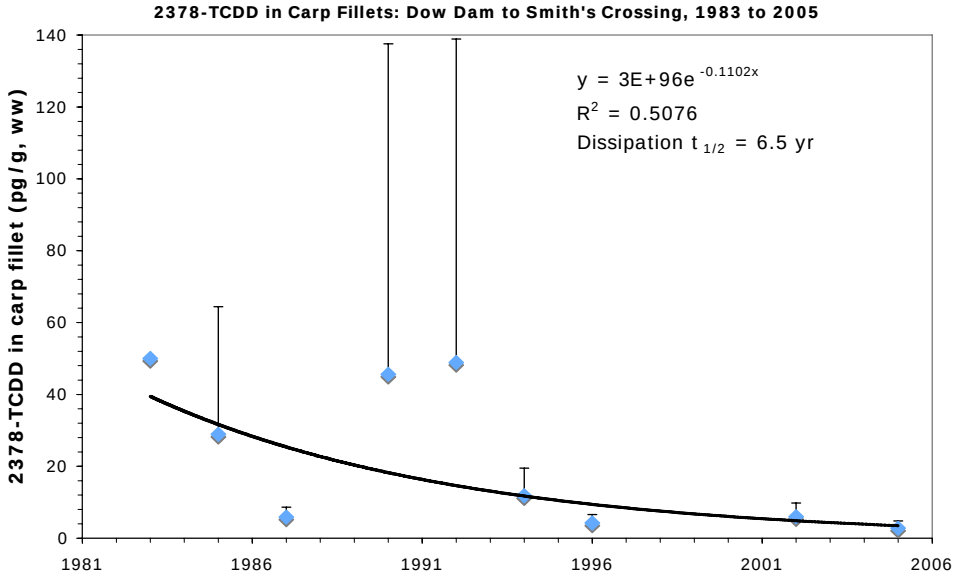


Figure 2. Time Trend Data for 2,3,7,8-TCDD in Native Carp Fillet Tissue Taken Downstream of the Dow Dam, 1983 to 2005.



2.0 SAMPLING DESIGN FOR COLLECTING FISH SPECIES, SIZE, AND CONCENTRATION DATA.

Development of the final fish sampling plan that is both site-specific, reasonable, and realistic will be carried out with input from the MDNR Scientists and Enforcement Officers, Field experts from the USFWS, local fishing guides, regional outdoors experts, and fishing clubs. The goal is to develop exposure information based on recent and comprehensive measurements rather than questionable data. In addition to collecting the relevant sized fish species, the study plan specifies fish preparation methods so that the HHRA can be based on actual amounts of TAs in fish fillets as consumed.

There are six major parameters that will be specified prior to the initiation of the field collection activities:

- Sampling site selection
- Target species (including alternate species, number of individuals, and size class)
- Number of replicate samples to be collected
- Target analytes
- Sampling times
- Sample field preparation and handling

These parameters will be documented on a field sample form prepared for each sampling location along the Tittabawassee River. The sample form will provide the sampling team with readily available information on the sampling objective, site location, site name/number, target species and alternate species to be collected, number and size range of individuals to be collected for each location, sampling and handling methods to be used, TAs to be evaluated, sampling date, and number of replicates to be collected. The sampling manager will retain the original sample forms and a copy kept with the field logbook.

2.1 Site Selection

Sampling sites along the Tittabawassee River will be selected to cover the potential bioaccumulation spectrum, ranging from near the Dow Chemical plant site to the confluence with the Saginaw River, and may include areas where existing data suggest sediment contamination might be likely. These would include areas of the river adjacent to areas of known flood plain soil contamination where erosion is likely, areas of the river where contaminated sediments accumulate and bioaccumulation potential might be enhanced (*i.e*., areas where water velocity slows and organic-rich sediments are deposited), or areas in which the intensity of sport fishing is high (*i.e*., public fishing areas). Modification of initial site selection may occur upon recommendation of local fishing experts as necessary. Ultimately, fish habitat where fishing is most likely to be successful will be considered when selecting fish sampling locations.

The procedures required to identify collection sites near point source discharges are usually straightforward. In this case, one sampling point will be located immediately

downstream of the Dow dam on the Tittabawassee River. It is often more difficult, however, to identify clearly defined candidate sites in areas affected by pollutants from non-point sources such as the flood plain soils along the Tittabawassee River. For this reason, the sampling locations will be initially selected from Midland down to the confluence of the Tittabawassee River with the Saginaw River. Three sampling locations will be selected based on their proximity to already selected surface water and sediment sampling sites. Locating fish sampling sites near the sites already selected for water and sediment sampling may allow the possibility of correlating contaminant concentrations in different environmental media (*i.e*., water, sediment, and fish). Bottom conditions, accessibility of the site, likely fish habitat, level of resource use by fishermen will also be considered in modifying or adding to these sampling locations in consultation with MDEQ. For Walleye, the Dow Dam may serve as the sole collection point in view of the migratory nature of Walleye into the Tittabawassee River during the winter spawn and their congregation at this physical barrier. It is assumed that Walleye collected in this location would reflect migratory Walleye along the entire stretch of the Tittabawassee River.

The final selection of both the number and location of sampling areas will also be based on availability of data on the indigenous fish communities and fishing activities since information on preferred feeding areas and migration patterns would aid in locating populations of the target species (Versar, 1982). Knowledge of habitat preference provided by MDNR fisheries biologists, Dow environmental scientists, and local fishermen will be used to improve the chances of locating suitable sampling locations for the various target species selected. This Study plans to consult with local fishermen, fishing guides, and MDNR representatives familiar with the Tittabawassee River in order to identify areas where the target species congregates for selection of the most appropriate sample collection points and to deploy the appropriate sampling equipment. Given the relatively short length of the Tittabawassee River from Midland to the confluence of the Saginaw River, accessibility to sampling locations is not considered a major issue; however, consideration will be given to the location of boat ramps and the depth of water required to deploy the selected sampling gear efficiently and safely.

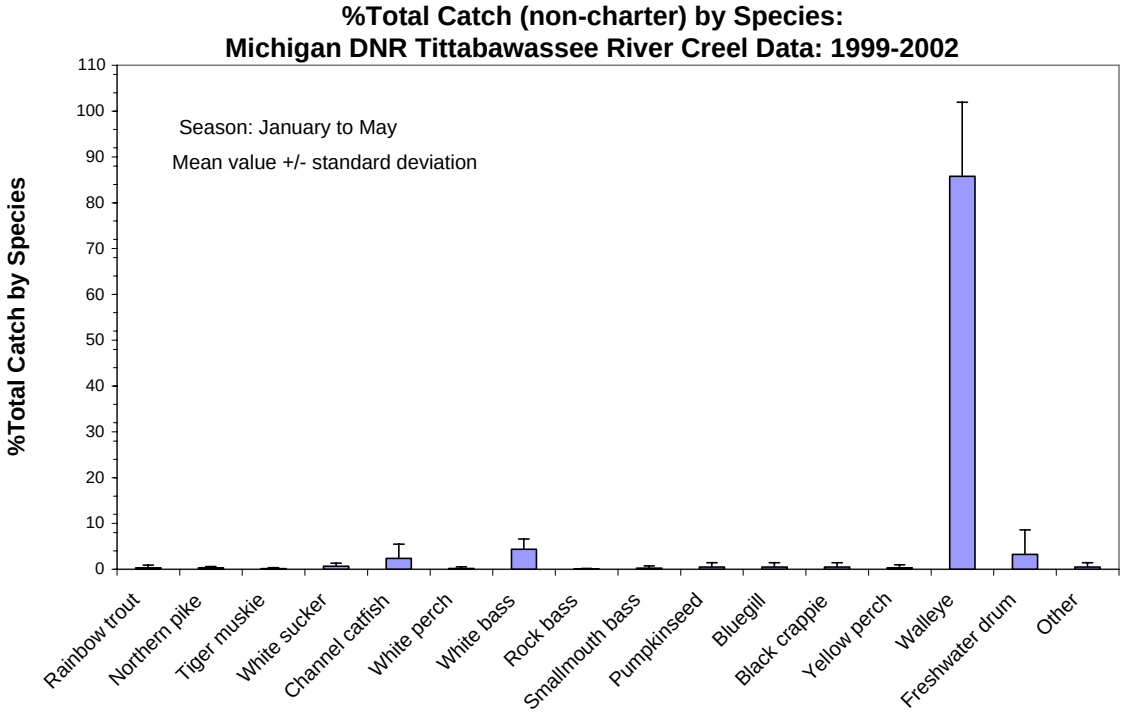
The final selection of each sampling site will be based on input from MDNR and other knowledgeable professionals. After the various sampling sites have been selected, they will be plotted and numbered on the existing Geographic Information System (GIS). The type of sampling to be conducted, water depth, and estimated time to the sampling site from an access point will be noted. The availability of landmarks for visual or range fixes will also be noted for each sampling location.

It is not thought that any threatened or endangered species covered under the Endangered Species Act (ESA) of 1973 exist within the waters of the Tittabawassee River. This issue will be reviewed with the MDNR and USFWS and if such a species does exist within the waterway, appropriate permits from the USFWS will be obtained. Additionally, any collection permits required by the State or Federal government for fish collection will be applied for in advance of sampling to ensure the sampling can be completed in a timely manner.

2.2 Target Species and Size Class Selection

The target species likely to be of interest for purposes of estimating human health risk will be identified along with the appropriate sampling sites. The primary selection criterion will be the target species that is commonly consumed locally and is of harvestable size. Creel survey data from 1999 to 2002 collected by the MDNR for the Tittabawassee River are shown in **Figure 3** (MDNR, unpublished data). These harvest data show that the majority of fish caught from the Tittabawassee River are Walleye (approximately 85%) during the active winter and spring fishing season. White Bass are next with about 4% of the catch, followed by Channel Catfish and Freshwater Drum at around 3% or less. The MDNR creel survey did not identify carp as a harvested species on the river. Whether such information is an artifact or represents fish catch and consumption profiles along the Tittabawassee River will be determined using the Activity Survey. Similar information from the second half of the year may also be desirable depending on Activity Survey information and the input from local experts on fishing. However, it should be noted that winter and spring fishing in the Tittabawassee River is more prevalent due to the Walleye spawning activity.

Figure 3. Creel survey data on the Tittabawassee River collected from January to May from 1999 to 2002, inclusive, by the Michigan DNR (Bay City office).



The final selection of target species will be determined based on the information derived from MDNR Creel survey data as well as identification of the primary sport-caught fish

consumed in the site-specific Activity Survey, the UMDES results, or other sources. It is anticipated that the focus of the fish sampling will be on Walleye although other species from different trophic levels such as Bass and Catfish will be included for completeness in the risk assessment process. Inclusion and collection of other species will be based on the professional judgment of MDNR scientists and field officers, the UMDES questionnaire, the HHRA Activity Survey, the current MDCH fish advisory and other sources of reliable information that can be verified.

Individual fish fillets will be collected from a number of fish species according to fishermen preference and size categories. A preliminary list of species, size categories and number of filets per size category are shown in the following table for purposes of discussion.

Table 1. Fish Sampling Plan by Species and Size

Target Species	Location	Size Class	# Fish Samples/Location	Total # of Fish/Size Class
Walleye	3	15 - 22 inches	10 - 20	30 - 60
		> 22 inches	10 - 20	30 - 60
White Bass	3	12 - 16 inches	10 - 20	30 - 60
		> 16 inches	10 - 20	30 - 60
Smallmouth Bass	3	12 - 16 inches	10 - 20	30 - 60
		>16 inches	10 - 20	30 - 60
Channel Catfish	3	12 - 24 inches	10 - 20	30 - 60
		> 24 inches	10 - 20	30 - 60

Based on a preliminary review of past fish sampling results for TCDD and PCDD/PCDF TEQs from the Tittabawassee River, the Coefficient of Variation (CV) for Walleye and other commonly-eaten fish at single locations does not exceed about 0.4 to 0.5, with corresponding logarithm of geometric standard deviation of about the same size. That means that a sample size of 10 per location would be sufficient to estimate the mean fish tissue concentration to within 10% to 20% at each location. If different locations have different concentrations (not expected for Walleyes, but possible for non-migratory fish, or perhaps for other PCOIs), the between-location variation will likely dominate uncertainty estimates for exposures due to fish ingestion, whereas for fish with common concentration distributions at different locations the samples taken at different locations can be combined. This suggests that uncertainties in fish tissue TA concentration will be a relatively small contributor to overall uncertainty in exposure estimates. The year-to-year variation also appears higher than the location-specific uncertainty in even the limited available data, and the uncertainty concomitant on that variation may dominate estimates of uncertainty for exposure-point fish concentrations. The CVs for carp tissue concentrations appear to be bigger, around 0.8 to 1; and the concentrations in carp are also larger as expected; however, carp are not commonly eaten, so even large uncertainties in their PCOI concentrations are unlikely to substantially affect uncertainties in exposure estimates.

A larger sample size is proposed in order to more firmly establish the distribution shape,

and the mean tissue concentration of the target fish that people eat. The purpose of this Study is to present the actual range of concentration to which the fishing-eating population is exposed as opposed to assuming that exposure would consist of lifetime consumption of the fish only at the extreme end of the concentration distribution. Other species and size categories may be added or changed in consultation with MDEQ based on Creel surveys, the site-specific Activity Survey, the UMDES results, or input from local fisheries experts.

2.3 Target Analyte Selection

At present, the primary focus of this sampling effort is to determine the concentrations, patterns, and variability of polychlorinated dioxins and furans (PCDD/Fs) in fish tissue collected from the Tittabawassee River. Other persistent pollutants (*i.e.*, PCBs, chlorinated pesticides, *etc.*) commonly found in fish tissue may be included in the analysis to provide context and additional information. If other TAs are identified in the course of the remedial investigation that might accumulate in fish tissue, these may be included in the analysis of the samples or replicate samples after consultation with MDEQ. Other data on water, sediment, and tissue contamination and priority pollutant scans from known point or non-point sources monitoring will also be reviewed to determine whether analysis of additional TAs is warranted before finalizing the analytical protocol.

2.4 Target Analyte Detection Limits

The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of the TAs. In the case of the PCDD/Fs, the detection limit selected is generally in the range of 0.1 parts per trillion (ppt) in view of the amount of tissue available for analysis. Non-detects will be handled as Limit of Detection (LOD) = 0.

2.5 Sampling Times

Sampling will be conducted during the period when the various target species are most frequently harvested (US EPA, 1989; Versar, 1982). The Walleye season and mid-Michigan fishing opportunities are concentrated in the winter to spring time period and in the fall for the Tittabawassee River. Exceptions to the sampling periods selected for the various species will be determined by input from MDNR or fishermen input that suggest alternative sampling periods would yield a better catch. The actual sampling period and the rationale for its selection will be documented fully and the final data report will include an assessment of sampling period effects on the results.

2.6 Sample Type and Preparation

Taxonomic identification will be performed and individual fish fillets will be obtained from the target species collected. Size is generally correlated with age, and older fish typically have higher concentrations of the TAs. The primary target size range ideally will include the typical harvestable range at each sampling site as well as fisherman preference for food quality (*i.e.*, male Walleye within a certain size range) (Phillips,

1980; Voiland *et al.*, 1991). The use of sizes of fish not usually caught or fish under the legal size limit might introduce more variability (*e.g.*, wider confidence intervals) and may not reflect the reality of the actual species and size most likely consumed. These sizes will be excluded from the sampling program for these reasons.

The preparation of the fillets from each fish collected will be done first to reflect the general practice among recreational fishermen. In this case, trimmed skinless fillets should be used for assessing exposure to members of the general population and most recreational fishers because few consumers of sport-caught fish eat the skin of the fish (US EPA, 2000). Preparation methods and other factors will be verified in the site-specific Activity Survey. Analysis of skinless fillets is also most appropriate for some target species such as catfish and other scale-less finfish species. This practice will also be verified using the site-specific Activity Survey. Because untrimmed skin-on fillets may be consumed by some segments of the population that use fish in stews or soups, the extent of this practice of preparation and cooking skin-on fillets will also be addressed in the Activity Survey. The second fillet from each fish will be retained as an untrimmed skin-on fillet, which will be held for possible future analysis if the Activity Survey indicates that a significant percentage of the users of this resource prepare their fish in this manner.

Whole individual fish collected as part of the sampling effort will be sorted by species, size, and location in accordance with sample handling procedures detailed in **Section 3.0**. The whole fish to be used in each sample will be wrapped individually, labeled, and bagged. These samples will then be taken to a clean room environment for further preparation. Because edible fillets furnish the data to be used in risk assessment, both sides of the whole fish will be filleted. One side will be prepared as a trimmed (*i.e.*, removal of the belly flap and lateral line), skin-off fillet, and used for the primary analysis. The other side will be prepared as an untrimmed, skin-on fillet, and preserved for possible future analysis. The individual fillet samples from each fish will be separately wrapped in aluminum foil, bagged and then wrapped together and re-labeled as to species, sample location, length and weight of fish that furnished the fillets. These samples will be placed on wet ice if transported to the selected analytical laboratory within 24 hours or frozen on dry ice if transport and delivery will not occur within that time period.

3.0 SAMPLE COLLECTION

The primary purpose of this sampling is to collect sufficient tissue from the edible portions of select fish species prepared in a manner relevant to human consumption that can be used to determine the concentration of congener-specific PCDDs, PCDFs, or other TAs and lipids. Sufficient muscle will be retained to analyze separately if needed or to conduct studies on the effects of cooking on the loss of TAs. Fish will be collected at various areas of the Tittabawassee River and will be harvested just prior to and during the appropriate fishing season, so that the sampling effort will represent normal sporting activities. The appropriate MDNR, MDEQ, and USFWS offices will be contacted well prior to any sampling activity to fulfill any permitting requirements. MDNR, MDEQ and USFWS will be notified of sampling dates and locations prior to actual sampling.

Sample collection activities will be initiated only after the fish tissue study plan is approved by MDEQ, and any permit requirements are met. This section details the overall sampling methodology, equipment and techniques to be employed in the fish sampling effort, considerations for ensuring preservation of sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation, and shipping. The sample collection will be conducted under a Scientific Collector's Permit obtained through the MDNR, if needed. The method of take will include standard electrofishing practices or possibly netting as necessary. All practices will be conducted in such a way to maximize public and worker safety.

For each fish harvested, the following field observations and measurements will be recorded:

- Sample ID
- Species
- General site description
- Photographs
- GPS coordinates
- Date and time of harvest
- Collectors initials

After recording observations and measurements, the sample will be processed as described below.

3.1 Sampling Equipment and Use

Fish contaminant data can best be compared when differences in taxa and size are minimized to the extent possible. Although various sampling equipment are routinely used to collect fish, electrofishing (or electroshocking) equipment and seines are the most commonly used collection methods in fresh water (Versar, 1982). Electrofishing is recommended for most fish sampling efforts because of its greater applicability and efficiency. Pulsed DC (direct current) electrofishing will be used in this sampling effort to obtain the samples of target fish species at each location. The proper scientific

collection permit(s) will be obtained before commencement of any electrofishing activities as previously noted.

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and will be described in the Health and Safety Plan. All field team members will be trained in electrofishing safety precautions and operation procedures. Each team member will be insulated from the water and the electrodes; therefore, chest waders and rubber gloves will be worn. Electrode and dip net handles will be constructed of insulating materials (*e.g.*, wood, fiberglass, etc.). Electrofishers/electrodes will be equipped with functional safety switches. Field team members will not reach into the water until the electrodes have been removed from the water or the electrofisher has been disengaged. At least two fish collection team members will be certified in CPR (cardiopulmonary resuscitation).

Many options exist for electrofisher configuration and field team organization; however, procedures will always involve a minimum two-person team for sampling streams and wadeable rivers. At least one biologist with training and experience in electrofishing techniques and fish taxonomy will be involved in each sampling event. Acceptable configurations of an electrofishing sampling program will be based on the conditions at the specific sampling location in the Tittabawassee River, but may include:

- Backpack electrofisher with two hand-held electrodes mounted on fiberglass poles. One crewmember, identified as the electrofisher unit operator, will carry the backpack unit and manipulate both the anode and cathode poles. The anode may be fitted with a net ring (and shallow net) to allow the unit operator to also net specimens. The remaining one or two team members will net fish with dip nets and are responsible for specimen transport and care in buckets or livewells.
- Backpack electrofisher with one hand-held anode pole and a trailing or floating cathode. The electrofisher unit operator manipulates the anode with one hand, and has a second hand free for use of a dip net. The remaining one or two team members again aid in the netting of specimens, and in addition are responsible for specimen transport in buckets or livewells.
- Tote barge electrofisher with two hand-held anode poles and a trailing/floating cathode (recommended for large streams and wadeable rivers). Two team members are each equipped with an anode pole and a dip net. Each is responsible for electrofishing and the netting of specimens. The remaining team member will follow, pushing or pulling the barge through the sample location. A livewell is maintained within the barge and/or within the sampling reach but outside the area of electric current.

The field equipment and supplies needed for fish sample collection may include:

- SOP for Fish Sampling
- Health and Safety Plan
- Boat and supplies
- Fuel supply (primary and auxiliary supply)

- Spare parts/repair kit
- Life preservers
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Spare oars
- Maps of sampling site locations
- Backpack or tote barge-mounted electrofisher
- Dip nets
- Block nets (*i.e*., seines)
- Buckets/livewells
- Elbow-length insulated waterproof gloves
- Chest waders (equipped with wading cleats, when necessary)
- Appropriate scientific collection permit(s)
- Polarized sunglasses
- Pencils, clipboard
- Global Positioning System (GPS) Unit
- Field logbook
- Recordkeeping/documentation supplies
- Copies of field protocols
- Sample request forms
- Specimen identification labels
- Chain-of-Custody (COC) Forms and COC tags or labels
- Indelible pens
- Sample processing equipment and supplies
- Holding trays
- Tape measure (100 m minimum)
- Fish Sampling Field Data Sheet
- Fish measuring board (500 mm minimum, with 1 mm increments)
- Calipers (metric units)
- Balance to weigh representative specimens for estimating tissue weight (metric units)
- Aluminum foil (extra heavy duty)
- Freezer tape
- String
- Several sizes of plastic bags for holding individual or composite samples
- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- Sample preservation and shipping supplies
- Ice (wet ice, blue ice packets, or dry ice)
- Ice chests
- Filament-reinforced tape to seal ice chests for transport to the central processing laboratory

3.2 Sample Location and Area

The exact location (*i.e.*, latitude and longitude) of the downstream and upstream limit of the sampling location will be recorded on each field data sheet. If a Global Positioning System unit is used to provide location information, the accuracy or design confidence of the unit will be noted. The sampling area will be determined by using either a standard length of stream (*e.g.*, a fixed-distance designation) or a standard number of stream channel "widths" may be used to measure the stream sampling area (*e.g.*, a proportional-distance designation-- 40 times the stream width is defined by Environmental Monitoring & Assessment Program [EMAP] for sampling (Lazorchak *et al.*, 1999). This latter approach allows variation in the length of the sampling area based on the size of the stream. Application of the proportional-distance approach in large streams or wadeable rivers may require the establishment of sampling program time and/or distance maxima (*e.g.*, no more than three hours of electrofishing or 500-meter length per sampling site).

3.3 Sampling Procedure

A. Collection via electrofishing will begin at the downstream limit of the sample location, and terminates at the upstream limit. Block nets will be set at the upstream and downstream ends of the sampling location prior to the initiation of any sampling activities. Fish collection commences at the downstream barrier. A minimum two-person fisheries crew proceeds to electrofish in an upstream direction using a side-to-side or bank-to-bank sweeping technique to maximize area coverage. All wadeable habitats within the area are sampled via a single pass, which terminates at the upstream barrier. Sampling efficiency is dependent, at least in part, on water clarity and the field team's ability to see and net the stunned fish. Therefore, each team member will wear polarized sunglasses, and sampling is conducted only during periods of optimal water clarity and flow. Fish are held in livewells (or buckets) for subsequent identification and enumeration.

B. All field equipment will be in good operating condition, and a plan for routine inspection, maintenance, and/or calibration will be developed to ensure consistency and quality of field data. Field data will be complete and legible, and will be entered on standardized field data forms. While in the field, the field team will have sufficient copies of standardized field data forms and chains-of-custody for all anticipated sampling sites.

C. All fish collected will be identified to species. Fish outside of the desired size class or target species are not included in the sample, and are released on site. A digital photograph will be taken of the specimen and weight, size, and gender recorded. The sampling team will record the location from which each fish was harvested based on maps and GPS information. Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time, and collector initials.

E. The individual fish will be bagged and transported to an interim holding facility for further processing according to the methods discussed below, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane before each fish is prepared.

F. The edible filet will be removed, weighed and then rinsed with nanopure water to remove any foreign debris that may have come into contact with the tissue during preparation. Approximately 1000 g of filets will be retained for analysis. For smaller fish it may be necessary to composite filets from the same species and sizes from the same area. A duplicate filet or filet composite will be preserved for possible studies of cooking loss or additional analyses.

G. The actual weights for each filet will be recorded in the appropriate field notebook and the filets will then be wrapped in aluminum foil transferred into a re-sealable and labeled plastic bags or single chemically clean, 1000-mL I-Chem jar.

H. Filet samples in labeled plastic bags or I-Chem jars will be immediately placed on ice and transported for homogenization and final processing.

I. Mops and bleach solution will be used to clean the interim preparation areas following daily activities.

3.4 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is preserved by prevention of loss of contaminants already present in the tissues and prevention of extraneous tissue contamination (Smith, 1985).

It is important to ensure the collection of live, intact fish for use in sample analysis for human risk assessment. Fish that have not been mutilated by the collection gear and that do not have any skin lacerations or fin deterioration that would allow body fluids to leak out of the specimen or contaminants to pass into the specimen after collection will be used. Fish that are found floating dead at a site will not be used for sample analysis for human risk assessments. For these reasons, US EPA (2000) recommends that any specimens that show any skin lacerations or fin deterioration of any kind not be used for human risk assessment. Once the samples have reached the laboratory, further care will be taken during thawing (if specimens are frozen) to ensure that all liquids from the thawed specimens are retained with the tissue sample as appropriate.

All potential sources of contamination in the field (*e.g.*, sampling gear, grease, spilled gasoline or diesel fuel, engine exhaust, dust, ice chests, and ice itself) will be identified

and appropriate steps taken to minimize or eliminate them. For example, during sampling, the boat will be positioned so that engine exhausts do not fall on the deck. Ice chests will be scrubbed clean with detergent and rinsed with distilled water after each use to prevent contamination. To avoid contamination from melting ice, samples will be placed in waterproof plastic bags (Stober, 1991). Sampling equipment that has obviously been contaminated by oils, grease, diesel fuel, or gasoline will not be used. All utensils or equipment that will be used directly in handling fish (*e.g*., fish measuring board or calipers) will be cleaned in the laboratory prior to each sampling trip, rinsed in acetone and pesticide-grade hexane, and stored in aluminum foil until used (Versar, 1982). Between sampling sites, the field collection team will clean each measurement device by rinsing it with ambient water and rewrapping it in aluminum foil to prevent contamination.

Ideally, all sample processing (*e.g*., filleting or resectioning) of collected fish will be performed at a sample processing facility under clean room conditions to reduce the possibility of sample contamination as noted above (Schmitt and Finger, 1987; Stober, 1991). If filleting fish must be performed in the field, a clean area will be set up away from sources of diesel exhaust and areas where gasoline, diesel fuel, or grease are used to help reduce the potential for surface and airborne contamination of the samples from PAHs and other contaminants. Use of a mobile laboratory or use of a portable resection table and enclosed hood would provide the best environment for sample processing in the field. If sample processing is conducted in the field, a notation will be made in the field records and on the sample processing record.

3.5 Field Recordkeeping

Thorough documentation of all field sample collection and processing activities is necessary for proper interpretation of field survey results. For fish contaminant studies, preprinted waterproof data forms, indelible ink, and writing implements that can function when wet will be used (Puget Sound Estuary Program, 1990). When multi-copy forms are required, no-carbon required (NCR) paper will be used because it allows information to be forwarded on the desired schedule and retained for the project file at the same time. The data collection phase includes the completion of a various sample-tracking forms, which includes information regarding the sample collection procedures. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel have been properly trained in these areas and perform these tasks in secured access facilities.

Field personnel will document all sampling activities in accordance with the Work Plan and SOPs. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing laboratory. These are 1) Field

record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) date and time of collection and (b) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

3.5.1 Field Record Form

The following information will be included on the field record for each sampling site as appropriate:

- Project number
- Sampling date and time
- Sampling site location and GPS coordinates
- Sampling depth (specify units of depth)
- Collection method
- Collectors' names and signatures
- Affiliation (including telephone number and address)

3.5.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format. The QA/QC samples will be labeled accordingly.

Each sample label will have a unique sample identification number consisting of: a two-letter prefix to distinguish the project ID, a 2-digit number to distinguish location, a two-letter abbreviation for the fish species, and a 2-digit number to designate fish number. In addition, tissue samples will be labeled ‘F’ for filet, accordingly. Field and laboratory blanks will be labeled with the project ID, date, and type of blank that are being collected. Example ID labeling schemes are illustrated below.

Example Fish Sample ID Labels

TR01WE01
TR = Tittabawassee River Project
01 = Location Reference
WE = Walleye; **CC** = Channel Catfish; **WB** = White Bass; **SM** = Smallmouth Bass;

NP= Northern Pike, etc.
01 = Fish number

TR01WE01F1
TR = Tittabawassee River Project
01 = Location Reference
WE = Walleye; **CC** = Channel Catfish; **WB** = White Bass; **SM** = Smallmouth Bass;
NP = Northern Pike, etc.
01 = Animal number
F = Filet tissue
1,2,3… = Replicate tissue sample number

TRMMDDBAB01
TR = Tittabawassee River Project
MMDD = Date (Month and Day only)
BAB = Blank sample type

- BAB = Fileting Atmospheric Blank
- BSR = Fileting Start Rinsate
- BER = Fileting End Rinsate
- HAB= Homogenate Atmospheric Blank
- HSR = Homogenate Start Rinsate
- HER = Homogenate End Rinsate

01 = Replicate number

A completed sample identification label will be taped to each container and the individual specimen will be placed in a waterproof plastic bag.

3.5.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual game specimen. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling date/time
- Processing and analysis requested
- Preservation method (wet/dry ice)

A completed sample identification label will be taped to each aluminum-foil wrapped specimen and the individual specimen will be placed in a waterproof plastic bag. After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual fish sample. Information on the COC label will also be recorded on the COC form.

3.5.4 Chain-of-Custody Form

Fish samples collected for analysis will be tracked in the field and in transit to the processing facility and then to the analytical laboratory. Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g*., ice chest) used. All pertinent information will be entered into the chain-of-custody form in the field including in-transit and laboratory delivery relinquishment/receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for tissue samples; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight, or locked in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

3.5.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, hydrologic conditions, weather conditions, boat or equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the fish contaminant monitoring data. This will also include method of fish capture, start time, ending time, duration of sampling, sampling location, and maximum and mean stream widths as well as sampling conditions (*e.g.*, visibility, flow, difficult access to stream, etc.).

3.6 Sample Field Handling

3.6.1 Species Identification

Qualified, trained fish biologists, familiar with the Tittabawassee River and target fish species, will conduct field identifications of collected fish. As soon as fish are removed from the collection device, they will be identified by species. Non-target species or specimens of target species that do not meet size requirements (*e.g.*, juveniles) will be returned to the water. When sufficient numbers of the target species have been identified to make up the sample for that location, the species name and all other appropriate information will be recorded on the field record forms. Samples will be properly preserved and labeled as discussed. Chain-of-custody forms will be used following sample preparation, and will include the same information as the sample labels.

3.6.2 Initial Inspection and Sorting

Individual fish of the selected target species and size will be rinsed in ambient water to remove any foreign material from the external surface. Small fish may be placed on ice immediately after capture to stun them, thereby facilitating processing and packaging procedures. Large fish will be stunned by a sharp blow with a wooden club or metal rod to the base of the skull. Care will be taken to keep the club reasonably clean to prevent cross-contamination of the samples (Versar, 1982). Once stunned, individual specimens of the target species will be grouped by species and general size class and placed in clean holding trays to prevent cross contamination. All fish will be inspected carefully to ensure that the sampling equipment has not damaged their skin and fins. Damaged specimens will be discarded (Versar, 1982).

3.6.3 Length or Size Measurements

Each fish within the selected target species will be measured to determine total body length (mm), and matched to the desired size class. To be consistent with the convention used by most fisheries biologists in the United States, maximum body length will be measured as the length from the anterior-most part of the fish to the tip of the longest caudal fin ray (when the lobes of the caudal fin are compressed dorsoventrally) (Anderson and Gutreuter, 1983).

3.6.4 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PCDD/PCDF congeners or TAs as if it were an actual sample. This meets US EPA's stipulation that field blanks should be submitted at a rate of five percent of the total number of samples. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for fish samples will consist of muscle homogenates from fish species collected

spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8- TCDF. Matrix spikes may also include PCBs or other TAs when appropriate for the intended analysis.

3.7 Sample Packaging

After initial processing to determine species, size, and sex, each fish will be individually wrapped in extra heavy-duty aluminum foil. The sample identification label will be taped to the outside of each aluminum foil package, each fish will be placed into a waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual specimens for the same species and size class from the sample location will be kept together (if possible) in one large waterproof plastic bag in the same shipping container (ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

3.8 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed. Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours (Smith, 1985; US EPA, 1990). If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer trailer unit will be used for temporary storage of fish samples at the interim processing location. Long-term storage of additional tissue or samples (until study termination) will take place at an off-site storage location yet to be determined. Tissue samples (in plastic bags or I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University where they will be stored at –20°C until homogenization. All samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures.

3.9 Sample Shipping

The fish samples will be hand-delivered or shipped to the processing location as soon as possible after collection and initial processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers

- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)
- PDA

Filets will be transported for final processing and homogenization within 48 hours. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

4.0 Laboratory Preparation

4.1 Sample Receipt and Chain-of-Custody

Fish samples will be shipped or hand-carried from the field and delivered to a processing location for filleting and further sample processing. Sample processing and distribution for analysis ideally will be performed by one processing location. Transportation of samples from the field will be coordinated between the sampling team supervisor and the supervisor responsible for sample processing and distribution. An accurate written custody record will be maintained so that possession and treatment of each sample can be traced from the time of collection through analysis and final disposition.

Fish samples will be brought (or shipped) to the sample processing location in sealed containers accompanied by a copy of the sample request form, a chain-of-custody form, and the field records. Each time custody of a sample or set of samples is transferred; the Personnel Custody Record of the COC form will be completed and signed by both parties. Corrections to the COC form will be made in indelible ink by drawing a single line through the original entry, entering the correct information and the reason for the change, and initialing and dating the correction. The original entry should never be obscured.

When custody is transferred from the field to the sample processing location, the following procedure will be used:

• Shipping time will be noted (has the shipping time exceeded the appropriate time for preservation method used?).
• Check that each shipping container has arrived undamaged and that the seals are intact.
• Open each shipping container and remove the copy of the sample request form, the COC form, and the field records.
• Note the general condition of the shipping container (samples iced properly with no leaks, etc.) and the accompanying documentation (dry, legible, etc.).
• Locate individual samples listed on the COC form and note the condition of their packaging. Individual specimens should be properly wrapped and labeled. Note any problems (container punctured, illegible labels, etc.) on the COC form.
• If individual samples are packaged together, check the contents of each composite sample container against the field record for that sample to ensure that the individual specimens are properly wrapped and labeled. Note any discrepancies or missing information on the COC form.
• Initial the COC form and record the date and time of sample receipt.
• Enter the following information for each composite sample into a permanent laboratory record book and, if applicable, a computerized database:

1 Sample identification number (specify conventions for specimen number)
2 Receipt date (YYYYMMDD)
3 Sampling date (YYYYMMDD)

4 Sampling site (name and/or identification number)
5 Fish species (scientific name or code number)
6 Total length of each fish (mm)

• If samples have been shipped on wet or blue ice, distribute them immediately to the technician responsible for sample preparation (*i.e.*, resection). If samples have been shipped on dry ice, they may be distributed immediately to the technician for processing or stored in a freezer at -20^{o} C for later processing. Once processed, fillets or edible portions of fish should be stored according to the procedures described below.

4.2 SAMPLE PROCESSING

Care will be taken during sample processing to avoid contaminating samples since Schmitt and Finger (1987) demonstrated that contamination of fish flesh samples is likely unless exacting clean dissection procedures are used. This may be particularly problematic for dioxins and furans, given the low levels that are of potential concern. Potential sources of contamination include dust, instruments, utensils, work surfaces, and containers that may contact the samples. All sample processing (*i.e.*, filleting) will be done in an appropriate laboratory facility under clean room conditions as previously noted (Stober, 1991). Clean rooms or work areas will be free of organic contaminants. Periodic wipe tests will be conducted in clean areas to verify the absence of significant levels of organic contaminants. All instruments, work surfaces, and containers used to process samples will be of materials that can be cleaned easily.

To avoid cross-contamination, all equipment used in sample processing (*i.e.*, filleting) will be cleaned thoroughly before each sample is prepared. Verification of the efficacy of cleaning procedures will be documented through the analysis of processing blanks or rinsates.

4.2.1 Samples for Organics Analysis

Tissue from the selected target fish species will be rinsed in nanopure water to remove any foreign material or blood from the external surface prior to and after filleting. Equipment used in processing samples for organics analysis will be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Filleting will be done on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy-duty aluminum foil that is changed after each filleting. Tissue will be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles (Lowenstein and Young, 1986). Fillets will be stored in heavy-duty aluminum foil.

Prior to preparing each fish filet sample, utensils and containers will be washed with detergent solution, rinsed with tap water, soaked in reagent-grade acetone or hexane, and rinsed with organic-free, distilled, de-ionized water. Work surfaces will be cleaned with reagent-grade acetone or hexane, washed with distilled water, and allowed to dry completely. Knives, fish scalers, measurement boards, etc., will be cleaned with reagent-

grade acetone or hexane followed by a rinse with contaminant-free distilled water between each fish sample (Stober, 1991).

All processed fish samples will be stored in pre-cleaned containers that are of sufficient size for sample content. All sample jars used are ordered as pre-cleaned and QA/QC grade. If jars are not pre-cleaned and QA/QC grade, then they will be cleaned in reagent grade acetone or hexane and rinsed with distilled water before use. After the jars have been dried, they will be sealed and stored until needed.

4.2.2 Processing Fish Samples

Processing in the laboratory to prepare fish fillet samples for analysis involves:

• Inspecting individual fish,
• Weighing individual fish,
• Scaling all fish with scales,
• Filleting with removal of skin, belly flap, and lateral line from one side; retaining skin, belly flap, and lateral line from the other side,
• Removal of skin of scaleless fish,
• Filleting with removal of belly flap and lateral line from one side; retaining belly flap and lateral line from the other side,
• Weighing individual fillets,
• Homogenizing sufficient tissue (*i.e.*, 200 gm) of trimmed, skin-off fillets and storing the homogenate in pre-screened borosilicate glass or polytetrafluoroethylene (PTFE) containers,
• Freezing appropriate aliquots for distribution to analytical laboratory, and
• Retaining remaining trimmed, skin-off fillet tissue and untrimmed, skin-on fillets for possible future analysis

Filets should be prepared within 48 hours of sample collection. Ideally, fish should not be frozen prior to filleting because freezing may cause internal organs to rupture and contaminate edible tissue (Stober, 1991; US EPA, 1986). However, if preparation cannot be performed within 48 hours, the whole fish should be frozen at the sampling site and shipped to the sample processing location on dry ice. Fish samples that arrive frozen at the sample processing location should be placed in a freezer for storage until filleting can be performed. The fish should then be partially thawed prior to preparation.

4.2.2.1 Sample Inspection

Individual fish received for filleting should be unwrapped and inspected carefully to ensure that they have been properly preserved during shipment and are otherwise uncompromised. Any specimen deemed unsuitable for further processing should be discarded and identified on the sample processing record.

4.2.2.2 Sample Weighing

A wet weight should be determined for each fish. All samples should be weighed on balances that are properly calibrated and of adequate accuracy and precision to meet program data quality objectives. Balance calibration should be checked at the beginning and end of each weighing session and after every 20 measurements. Fish shipped on wet or blue ice should be weighed directly on a foil-lined balance tray. To prevent cross contamination between individual fish, the foil lining should be replaced after each weighing. Frozen fish (*i.e.*, shipped on dry ice) should be weighed in clean, tared, non-contaminating containers if they will thaw before the weighing can be completed. All liquid from the thawed whole fish sample will be kept in the container as part of the sample. All weights should be recorded to the nearest gram on the sample processing record and in the laboratory notebook.

4.2.2.3 Scaling or Skinning

To control contamination, separate sets of utensils and cutting boards will be used for skinning or scaling fish and for filleting fish. Fish with scales will be scaled and any adhering slime removed prior to filleting. For these fish, one fillet will be prepared trimmed (belly flap and lateral line removed) and skin-off. The other will retain the belly flap, lateral line, and skin. Only the trimmed, skin-off fillet will be analyzed initially. Fish without scales (*e.g.*, catfish) will be skinned prior to filleting. These fillet types are selected as the fillet or sample type most appropriate for each target species based on the dietary customs of local populations of sport-fish consumers (US EPA, 2000).

A fish is scaled by laying it flat on a clean glass or PTFE cutting board or on one that has been covered with heavy duty aluminum foil and removing the scales and adhering slime by scraping from the tail to the head using the blade edge of a clean stainless steel, ceramic, or titanium knife. Cross-contamination will be controlled by rinsing the cutting board and knife with contaminant-free distilled water between fish. If an aluminum-foil-covered cutting board is used, the foil should be changed between fish. The skin should be removed from fish by loosening the skin just behind the gills and pulling it off between knife blade and thumb or with pliers. Once the scales and slime have been scraped off and the skin removed, the outside of the fish should be washed with contaminant-free distilled water and it should be placed on a second clean cutting board for filleting.

4.2.2.4 Filleting

Filleting should be conducted only by or under the supervision of an experienced fisheries biologist. Talc- or dust-free gloves made of non-contaminating materials may be used if desired. Prior to filleting, hands should be washed with soap and rinsed thoroughly in tap water, followed by distilled water (US EPA, 1991). Specimens should come into contact with non-contaminating surfaces only. Fish should be filleted on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy-duty aluminum foil that is changed between fish (Puget Sound Estuary Program, 1990a, 1990b). Care must be taken to avoid contaminating fillet tissues

with material released from inadvertent puncture of internal organs. If materials released from the inadvertent puncture of the internal organs during re-sectioning contaminate the fillet tissue, it will be eliminated as a sample. A notation will be made in the sample processing record of any discarded sample.

Ideally, fish should be filleted while ice crystals are still present in the muscle tissue. Therefore, if fish have been frozen, they should not be allowed to thaw completely prior to filleting. Fish should be thawed only to the point where it becomes possible to make an incision into the flesh (US EPA, 1991). Clean, high-quality stainless steel, ceramic, or titanium utensils should be used to remove one or both fillets from each fish, as necessary.

The belly flap and lateral line will be included only on the skin-on fillet that is retained for possible future analysis. Any dark muscle tissue in the vicinity of the lateral line should not be separated from the light muscle tissue that constitutes the rest of the muscle tissue mass. Bones still present in the tissue after filleting should be removed carefully (US EPA, 1991). Both fillets are removed from each fish as noted, but only a portion of the trimmed skin-off fillet will subject to analysis. The untrimmed skin-on fillet and remaining trimmed skin-off fillet will be retained for possible future analysis or cooking loss studies. Fillets should be weighed individually, and the weight(s) recorded to the nearest gram on the sample processing record.

Portions of the trimmed, skin-off fillets are to be homogenized immediately. Approximately 200 grams (gm) of the trimmed, skin-off fillet will be placed in a properly cleaned glass or PTFE homogenization container. To facilitate homogenization, it may be necessary or desirable to chop the 200 gm of the fillet into smaller pieces using a titanium or stainless steel knife prior to placement in the homogenization container. The remaining trimmed skin-off and untrimmed skin-on fillets will be wrapped in heavy-duty aluminum foil and labeled with the sample identification number, the sample type (e.g., "F" for fillet), the weight (g), the date of resection, and the designation "F1" for trimmed skin-off and "F2" for untrimmed skin-on should be added to the sample identification number for each fillet. The individual fillets from each fish should be kept together and stored frozen until needed.

4.2.2.5 Preparation of Individual Homogenates

A. Tissue samples received from the processing location will be stored at –20°C until they are ready for homogenization. Replicate samples or samples not immediately needed for sampling will be stored under the same conditions.

B. To ensure even distribution of contaminants throughout tissue samples and to facilitate extraction and digestion of samples, a minimum 200 gm portion of each fillet will be ground and homogenized prior to analysis. Fish fillets should be ground and homogenized using an automatic grinder or high-speed blender or homogenizer. Grinding and homogenization of tissue is easier when it is partially frozen (Stober, 1991). Chilling the grinder/blender briefly with a few chips of dry ice may also help keep the tissue from sticking to it (Smith, 1985). The fillet sample will be ground until it appears

to be homogeneous. The ground sample should then be divided into quarters, opposite quarters mixed together by hand, and the two halves mixed together. The grinding, quartering, and hand-mixing steps should be repeated at least two more times. If chunks of tissue are present at this point, the grinding and homogenization will be repeated. The sample processing location will prepare aliquots of the individual homogenates for analysis, distribute the aliquots to the appropriate laboratory, and archive the remainder of each homogenate along with the remaining tissue. Before, during, and after sample preparation, blenders will be washed with Liquinox soap, rinsed three times with nanopure water, and reagent grade acetone and hexane rinsed. Other equipment and surfaces that may potentially contact the sample will be likewise cleaned regularly. Verification of the efficacy of cleaning procedures may be documented through the analysis of processing blanks or rinsates.

C. The preparation of each individual homogenate will be noted on the sample processing record. The actual sample size required will depend on the analytical method used and the laboratory performing the analysis. Therefore, the exact sample size required for each type of analysis will be determined in advance with the analytical laboratory selected. Homogenates will be aliquoted into four to six separate chemically clean I-CHEM jars and frozen. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Sample IDs will be labeled for each replicate homogenate sample that is archived along with the remaining fillets.

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory. The frozen aliquot(s) will be transferred on dry ice to the analytical laboratory accompanied by a sample transfer record. The sample transfer record will include a section that serves as the analytical laboratory COC record. The COC record will be signed each time the samples change hands for preparation and analysis.

E. Care will be taken during all sample processing to avoid contaminating samples. This may be particularly problematic for PCDDs and PCDFs, given the low levels that are of potential concern. Potential sources of contamination include dust, instruments, utensils, work surfaces, and containers that may contact the samples. All sample processing will be done in an appropriate laboratory facility under clean room conditions. Clean rooms or work areas will be free of organic contaminants. Periodic wipe tests may be conducted in clean areas to verify the absence of significant levels of organic contaminants. All instruments, work surfaces, and containers used to process samples will be of materials that can be cleaned easily.

F. All laboratory practices will be recorded in the appropriate laboratory notebook.

4.3 Sample Shipping to Analytical Laboratory

Tissue homogenates, field blanks, and MS/MSD samples will be packaged and shipped for laboratory analysis according to US EPA/REAC guidelines (US EPA, 1994) as noted above.

Shipping materials needed include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)
- PDA

Samples will be transported to the analytical laboratory as soon as feasible after processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the analytical laboratory unless prior plans for such a delivery have been agreed upon with the laboratory staff. The time the samples were collected and time of their arrival at the analytical laboratory will be recorded on the COC form.

4.4 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD, PCDF, or other TA detected across species, sizes, and sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, date and time of sample collection, sample and tissue type, lipid content of tissues, TA tissue concentrations, and treatment of LOD in non-detects. The data entry will be verified to ensure the accuracy of the information. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

4.5 Data Analysis

The objective of data analysis is to identify and report the TA concentrations measured in fish species that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error), and develop a valid PDF for use in exposure and risk assessment. These steps are outlined in the Exposure Assessment Work Plan currently under development. Ultimately, this information will be used to assess the potential risk of TA exposure from consumption of fish to humans.

5.0 References

Anderson, R.O., and S.J. Gutreuter. 1983. Length, weight, and associated structural indices. pp. 283-300. In: *Fisheries Techniques*. L.A. Nielson and D.L. Johnson (eds). American Fisheries Society, Bethesda, MD.

Lazorchak JM, Klemm DJ, and Peck DV, 1999. Environmental Monitoring and Assessment Program: Surface Waters: Field Operations and Methods Manual for Measuring the Ecological Condition of Wadeable Streams. US Environmental Protection Agency, Environmental Monitoring and Assessment Program. Washington, DC. NTIS/PB99-139156.

Lowenstein, G.G., and D.R. Young. 1986. *National Status and Trends Program for Marine Environmental Quality, Benthic Surveillance Project: Cycle III Field Manual*. NOAA Tech. Memorandum NOS OMA 28. National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Rockville, MD.

Phillips, D.J.H. 1980. *Quantitative Aquatic Biological Indicators.* Pollution Monitoring Series. Applied Science Publishers Ltd, London, England.

Puget Sound Estuary Program. 1990a (revised). Recommended protocols for station positioning in Puget Sound. In: *Recommended Protocols and Guidelines for Measuring Selected Environmental Variables in Puget Sound*. Prepared by PTI Environmental Services, Bellevue, WA. Region 10, U.S. Environmental Protection Agency, Seattle, WA.

Puget Sound Estuary Program. 1990b (revised). Recommended protocols for sampling soft-bottom demersal fishes by beach seine and trawl in Puget Sound. In: *Recommended Protocols and Guidelines for Measuring Selected Environmental Variables in Puget Sound*. Prepared by PTI Environmental Services, Bellevue, WA. Region 10, U.S. Environmental Protection Agency, Seattle, WA.

Schmitt, C.J., and S.E. Finger. 1987. The effects of sample preparation on measured concentrations of eight elements in edible tissues of fish from streams contaminated by lead mining: *Arch. Environ. Contam. Toxicol.* 16:185-207.

Smith, R.L. 1985. *Guidance on Sampling Aquatic Organisms for Tissue Analyses during FY 1986*. Environmental Services Division, Region 3, U.S. Environmental Protection Agency, Philadelphia, PA.

Stober, Q.J. 1991. *Guidelines for Fish Sampling and Tissue Preparation for Bioaccumulative Contaminants*. Environmental Services Division, Region 4, U.S. Environmental Protection Agency, Athens, GA.

US EPA, 1986. *Bioaccumulation Monitoring Guidance: 4. Analytical Methods for U.S. EPA Priority Pollutants and 301(h) Pesticides in Tissues from Marine and Estuarine Organisms*. US Environmental Protection Agency. EPA-503/6-90-002. Office of Marine and Estuarine Protection, Washington, DC.

US EPA, 1989. *Analytical Procedures and Quality Assurance Plan for the Determination of Xenobiotic Chemical Contaminants in Fish*. US Environmental Protection Agency. EPA-600/3-90-023. Environmental Research Laboratory, Duluth, NM.

US EPA, 1990. *Work Plan for FY 91 Regional Ambient Fish Tissue Monitoring Program Activity No. ELR 80*. US Environmental Protection Agency. Environmental Monitoring and Compliance Branch, Region 7, Kansas City, KS.

US EPA, 1991. *Environmental Monitoring and Assessment Program (EMAP) Near Coastal Program Laboratory Methods for Filleting and Compositing Fish for Organic and Inorganic Contaminant Analyses.*

Draft. US Environmental Protection Agency. Office of Research and Development, Environmental Research Laboratory, Narragansett, RI.

US EPA, 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories Volume 1 Fish Sampling and Analysis Third Edition. United States Environmental Protection Agency, Office of Water (4305). EPA 823-B-00-007. November 2000. Washington, D.C

Versar, 1982. *Sampling Protocols for Collecting Surface Water, Bed Sediment, Bivalves and Fish for Priority Pollutant Analysis—Final Draft Report.* EPA Contract 68-01-6195. Prepared for Office of Water Regulations and Standards, U.S. Environmental Protection Agency. Springfield, VA.

Voiland, M.P., K.L. Gall, D.J. Lisk, and D.B. MacNeill. 1991. Effectiveness of recommended fat-trimming procedures on the reduction of PCB and Mirex levels in Brown trout (*Salmo trutta*) from Lake Ontario. *J. Great Lakes Res.* 17(4):454-460.

Game Tissue Study Plan

Study Objectives

1. To identify and collect an adequate number of those species of game (*i.e.*, deer, turkey, rabbits, and other species) from areas along the Tittabawassee River most commonly caught and consumed by hunters,
2. To identify and sample those locations along the Tittabawassee River locations, in which the targeted game species most likely occur and which are most commonly and legally hunted,
3. To identify the appropriate collection times for the selected game species and implement the sampling at that time,
4. To identify and prepare individual edible portions for analysis in the same manner as is commonly done by consumers of game from along the Tittabawassee River, and
5. To submit those game tissue samples to a qualified laboratory for analysis of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans (PCDD/Fs) relevant to the Tittabawassee River Study Area.

Tissue from the game sampling will be preserved in the event that additional or confirmatory analysis is required. The analytical results from the game tissue sampling will be used to estimate the probability density function (PDF) for concentration used to estimate PCOI exposure through ingestion of various game species. The necessary data inputs, methods and decisions used to create this specific PDF will be detailed in the Exposure Assessment Work Plan. Other aspects of (PCDD/Fs) exposure through game ingestion, such as weighting the take of game from various areas, consumption of specific game species, accounting for cooking loss of (PCDD/Fs), and determining the frequency and rate of consumption will also be detailed in the relevant Exposure Assessment Work Plan currently under development.

The sampling plan and methods for acquiring qualitative and quantitative data on the species and seasonal aspects of game caught for consumption by licensed hunters in the Tittabawassee River Study Area will be developed in part from hunting regulations and information collected by the MDNR or other sources of information such as the planned Activity Survey, the University of Michigan Dioxin Exposure Survey (UMDES) questionnaire information, local hunting ordinances, or additional, focused hunting surveys developed to fill relevant data gaps that are identified. Experts on hunting in the Tittabawassee River (*i.e.*, MDNR, U.S. Fish and Wildlife [US FWS], local hunters and outdoors guides, etc.) will also be interviewed to ensure that the sampling effort is site-specific and relevant. Any suggested modifications relevant to this plan in terms of species, numbers, and preparation methods based on their inputs will be adopted in order to improve the relevance, accuracy, and site-specificity of the game sampling protocol, thereby further reducing uncertainty. Planning and documentation of the sampling procedures will be done to ensure that collection activities are time and labor-effective and that sample integrity is preserved. It is anticipated that both collection and analysis

of game tissue can be completed within 12 months following approval of this work plan by MDEQ.

1.0 Introduction

Dow previously undertook a study to assess the potential for human exposure to PCDD/Fs from wild game harvested within the Tittabawassee River Study Area. Tissue from selected game species was collected in the fall of 2003 and analyzed for PCDD/Fs.

This study revealed that selected species of game collected along the Tittabawassee River downstream of the Dow plant had higher residual levels of PCDD/Fs than the same species collected upstream of the Dow plant. Consumption advisories for these game species have been issued by the State of Michigan on the basis of these findings; however, the small sample size of the wild game study, the impact of dietary substitution of wild game for meats and protein sources that also contain dioxins, the issue of cooking loss and uncertainty over potential human exposure makes it difficult to draw firm conclusions about the actual human health risks posed by these results. Nonetheless, since game from the Tittabawassee River Study Area may be consumed by hunters, their families, and others, ingestion of game may constitute a completed exposure pathway and requires inclusion and evaluation in the Human Health Risk Assessment (HHRA).

In order to augment the available wild game data and to provide site-specific information for the HHRA concerning the types and number of wild game species harvested from the Study Area, this Study proposes to carry out sampling to collect additional game tissue samples for analysis based on species preferentially harvested by hunters in the areas most commonly and legally hunted, and prepared for analysis in the manner most common to these groups as revealed by a planned Activity Survey. This information will be supplemented by interviews with local hunting experts and the Michigan Department of Natural Resources (MDNR). This work plan is based on modifications to the pre-existing work plan developed by ENTRIX (2003) and details the methods for collecting, preserving, and shipping game tissue from the Tittabawassee River Study Area to a laboratory for analysis of (PCDD/Fs) in the edible portions of local game.

2.0 SAMPLING DESIGN FOR COLLECTING GAME SPECIES CONCENTRATION DATA.

Development of the final game sampling plan that is site-specific, reasonable, and relevant will be based on input from the MDNR Scientists and Enforcement Officers, Field experts from the US FWS, local hunters and guides, regional outdoors experts, and hunting clubs. In addition to collecting the relevant game species, the study protocol provides recommendations on preparing game so that the HHRA can be based on actual amounts of PCDD/Fs in game consumed by hunters and others. The primary considerations for this sampling effort are public safety, collection of a representative and robust set of game tissue samples, and chain-of-custody and sample integrity issues.

There are six major parameters that will be specified prior to the initiation of the field collection activities:

- Site selection
- Target species
- Target analytes (PCDD/Fs)
- Target analyte screening values
- Sampling times
- Sample type

These parameters will be documented on a sample form prepared for each sampling location along the Tittabawassee River. The sample form will provide the sampling team with readily available information on the sampling objective, site location, site name/number, target species to be collected, number of individuals to be collected for each location, sampling and field preparation method to be used, target analytes (PCDD/Fs) to be evaluated, sampling date, and number of replicates to be collected. The sampling manager will retain the original sample forms and a copy will be kept with the field logbook.

2.1 Site Selection

Sampling sites for game along the Tittabawassee River will be selected from within the area from near the Dow Chemical plant site to the confluence with the Saginaw River. The final sampling sites will be selected based on local ordinances and regulations, as well as locations in which hunting is most likely to occur (*e.g.*, the Shiawassee National Forest) and may include areas where existing environmental data suggest contamination might be likely, if hunting is not restricted by ordinance in those areas. These would include areas along the river where soil contamination is likely and areas in which local ordinances and state regulations allow hunting and the hunting intensity is high. Modification of initial site selection may occur upon recommendation of local hunters or hunting experts as necessary. Ultimately, areas of game habitat that hunters most frequently use is likely to provide the best measure of potential exposure to consumers of game and will be given priority when selecting game sampling locations.

The procedures required to identify game collection sites will be straightforward. All sampling will be conducted downstream of Midland and in areas where hunting is allowed by ordinance and regulation. For any new species selected for this study, it will be necessary to obtain control (upstream animals) for general comparison purposes. Currently, the control (upstream) tissue data for deer, turkey and squirrel are sufficient for this comparison. Of special interest will be the Shiawassee National Forest in which deer hunting is allowed; however, additional locations will be chosen based on responses to the Activity Survey as well as information gathered by the UMDES, provided by MDNR or local hunting experts. Accessibility of the site, likely game habitat, level of resource use by hunters, and regulations will also be considered in modifying or adding to these sampling locations. Soil or sediment sampling points near each game sampling point will be identified and the results evaluated to examine the possibility of correlating contaminant concentrations between different environmental media (*i.e.*, soil, sediment, and game). If no soil or sediment sampling points exist in or near the game sampling location, additional soil or sediment samples will be collected for comparison.

The final selection of both the number and location of sampling areas will also be based on availability of data on the indigenous game communities and hunting activities since information on preferred feeding areas, migration patterns, and hunting areas would aid in locating populations of the target species. Knowledge of habitat preference provided by MDNR game biologists, Dow environmental scientists, and local hunters will be used to improve the chances of locating suitable sampling locations for the various target species selected. This Study plans to consult with local hunters, guides, and MDNR representatives familiar with game within the Tittabawassee River Study Area in order to identify areas where the target species congregates and hunting occurs for selection of the most appropriate sample collection areas.

The final selection of each sampling site will be based on the best professional judgment of the field sampling staff and input from MDNR and other knowledgeable professionals. Once the various sampling sites have been selected, they will be plotted and numbered on the existing Geographic Information System (GIS) using a Global Positioning System (GPS) for precise location. The type of sampling to be conducted and estimated time to the sampling site from an access point will be noted. The availability of landmarks for visual or range fixes will also be noted for each sampling location.

Prior to sampling it will be determined if the areas are inhabited by any threatened or endangered species covered under the Endangered Species Act (ESA) of 1973. A complete listing of the current status of all threatened and endangered species is available on-line on the US FWS website**.** If such a species does exist within the proposed sampling area, appropriate permits from the US FWS will be obtained or an alternate sampling location selected. Additionally, any collection permits required by the State or Federal government will be applied for in time for sample collection.

2.2 Target Species Selection

The three species initially selected for this site-specific study are the same as proposed for inclusion in the original game sampling program: white-tailed deer (*Odocoileus*

virginianus), wild turkey (*Meleagris gallopavo*) and cottontail rabbit (*Sylvilagus floridanus*). Since squirrels were substituted for rabbits in the first wildgame study, it will be necessary to include an upstream control sample for rabbits. If rabbit remain elusive in the Study Areas, squirrels will be again be used as substitutes. These species were selected due to their presence within the Tittabawassee River Study Area and the fact that they are resident game species that may be commonly hunted within the Study Area. White-tailed deer, wild turkey, and cottontail rabbit are herbivores that are resident species in the region that make them a good indicator of conditions within the Study Area. Deer are a particularly important game species because they are heavily hunted and a single deer can provide multiple meals.

The final selection of target species will be determined based the information derived from MDNR information as well as identification of the primary game taken and consumed in the site-specific Activity Survey or other sources. It is anticipated that the primary focus of the game sampling will be on deer although other species will be included for completeness in the risk assessment process. Inclusion and collection of other species will be based on the professional judgment of MDNR scientists and field officers, the UMDES questionnaire, the HHRA Activity Survey, local hunters or guides, and other sources of reliable information that can be verified.

Individual samples will be collected from the targeted game species in the selected sampling sites (which will be chosen as distinct from those already sampled since the initial sampling gives a good estimate of concentrations in those areas for deer and turkey). In general, muscle tissue will be collected in sufficient amounts to allow retention of tissue for additional analysis as needed. In the case of deer, certain other tissues or organ meats (*i.e*., fat, liver, kidney, heart, brain, etc.) will also be collected for possible analysis if such tissues are utilized by specific segments of the population. Which organs are analyzed for PCDD/Fs will be determined by the Activity survey and other information collected locally. A preliminary list of species and number of samples per species are shown in the following table.

Table 1. Game Sampling Plan by Species

Target Species	Location	Sample type	# Tissue Samples/Location	Total # of Samples
White-tailed Deer	4	Muscle, organs	10-15	40 - 60
Wild Turkey	4	Muscle	10-15	40 - 60
Cotton-tail Rabbit	4	Muscle	15 - 50	45 - 150

The number of samples for rabbits will be adjusted in a gradient down the river (based on the gradient of variation in concentrations observed in squirrels). The numbers of tissue samples given are adequate to obtain estimates of mean concentration with an uncertainty of about 20%, based on the initial sampling data, and also allow adequate specification of the distribution. Other species/sample numbers may be changed based on the site-specific Activity Survey or input from local hunters or guides and MDNR experts.

2.3 Target Analyte Selection

At present, the primary focus of this sampling effort is to determine the concentrations, patterns, and variability of polychlorinated dioxins and furans (PCDD/Fs) in game tissue collected from along the Tittabawassee River. Other persistent pollutants (*i.e.*, PCBs, chlorinated pesticides, metals etc.) commonly or previously found in game muscle tissue or organs may be included in the analysis to provide context and additional information.

2.4 Target Analyte Detection Limits

The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of (PCDD/Fs) in select tissue samples from wild game animals collected from various locations on along the Tittabawassee River. In the case of congener-specific PCDD/Fs, the detection limit selected is generally in the range of 0.1 part per trillion (ppt) in view of the amount of tissue available for analysis (results to be reported on a wet weight and lipid-adjusted basis). Non-detects will be handled as Limit of Detection (LOD) = 0.

2.5 Sampling Times

Sampling will be conducted during the period when the various target species are most frequently harvested. Therefore, this sampling activity will coincide with the harvesting of edible portions of deer, turkey, and rabbits by hunters along the Tittabawassee River during the late fall hunting season of 2006. The sampling locations will be sampled until the targeted sample size for each species is attained. Possible exceptions to the recommended sampling periods for different game species will be determined by information gathered by the Activity survey or other sources of site-specific information or input from MDNR and local hunters that suggest alternative sampling periods should be used. Therefore, the entire sampling effort will be dependent on the presence or abundance of the target species at each site, sampling period, weather conditions, and sampling success. The actual sampling period and the rationale for its selection will be documented fully and the final report will include an assessment of sampling period effects on the results.

2.6 Sample Type and Preparation

Individual samples of edible muscle or organ tissue will be obtained and analyzed based on the target species selected. The sampling objectives are dependent on the targeted species.

For white-tailed deer, the objective will be to harvest a representative sample of male and female deer that are within the age group most targeted by hunters that hunt animals from along the Tittabawassee River. Relative to age, every effort will be made to avoid fawns and to try to harvest a similar age structure among locations. However, it may not be possible to match all possible variables. The potential influences of variables such as age, weight and gender will be evaluated once the samples are analyzed (evaluation of the initial sampling indicated that any differences with sex or age were small compared

with differences between locations) and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For wild turkey, the objective is also to collect a representative sample of both male and female turkey that would best represent a typical harvest by hunters using these locations since the fall hunt allows hunters to hunt either sex. The decision to collect both sexes for deer and turkey is also based on past discussions with MDEQ, USFWS, and MDNR in order to evaluate whether there are gender-specific differences in concentrations of TEQs. Again, the potential influences of variables such as age and gender will be evaluated once the samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For rabbit, the sampling may be more opportunistic rather than targeted in that sex will not be a determinant in the collecting of animals from each location. In the event that rabbits are not abundant as occurred during the initial game study, it may be once again necessary to substitute squirrels in place of rabbits. If rabbits can be collected, it will be necessary to add an upstream sample as well. If squirrels are selected, a single species present in the study areas will be targeted for collection. As with deer and turkey, the potential influences of variables such as age and gender will be evaluated once the samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

The preparation of the samples from each game animal collected will be done to reflect the general practice among hunters and will reflect as well the preparatory steps prior to cooking. In the case of deer and rabbit, trimmed skinless muscle meat should be used for assessing exposure to members of the general population and most hunters since consumers of deer or rabbit do not eat the skin. Samples of turkey will be prepared with the skin on and skin off. Preparation methods for various game species and other factors that might influence residues will be verified in the site-specific Activity survey. The consumption or use of other tissues (*i.e.*, organ meats) by some segments of the population will also be determined in the site-specific Activity survey. Analysis of organ meats will occur only if these tissues are consumed or used by the populations in question. A sufficient amount of tissue from each game animal harvested will be retained for possible additional analysis if cooking loss needs to be ascertained or other analysis is required for purposes of ascertaining or refining exposure estimates.

Whole game animals collected as part of the sampling effort will be sorted by species, size, gender, and sample location in accordance with sample handling procedures detailed below. After samples have been collected and initial documentation has been completed, samples will be initially processed at a secured field facility to avoid contamination with soil or sediments. In this facility, wild game specimens will be dressed according to standard hunting practices.

For deer, it is this Study's intention to utilize the deer hunter population directly in the collection of tissue and organ samples, if possible. During the fall hunt, this Study will locate a preparation area in or near each of the sample locations and offer to dress the deer taken in exchange for a sample of muscle tissue and select organs. Some form of

monetary compensation may be offered to individual deer hunters as well. Providing a cleaning service will minimize external contamination and allow standardization of the individual sample collected in terms of amount and location. For each deer, the approximate size, weight, and age of the deer will be recorded. Certain tissues (*i.e.*, fat from the hide, kidney, liver, heart, brains, etc.) that are removed as part of the dressing procedure will be retained (provided the hunter permits this). The exterior of all tissues harvested will be rinsed with distilled water to remove foreign debris, fur, etc. Depending on the size of the tissues available, up to 1000 g will be cut into small cubes (approximately 1 cubic inch), weighed, and transferred into a chemically clean, 1 L I-CHEM jar.

Deer muscle tissue will be collected after skinning. Some edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area. The exterior of all muscle harvested will again be rinsed with distilled water to remove foreign debris, fur, blood, etc. Each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and then transferred into a pre-labeled, chemically clean, 1000-mL I-Chem jar. A duplicate set of samples will be collected and retained for possible evaluation of cooking loss. All of the tissue and muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or a similar facility. At this facility, samples will be stored at -20^{o}C where a subset will be homogenized. Once homogenized, the samples will be separated into six aliquots and transferred into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived at the URCF. Splits will be made available to MDEQ upon request.

For turkey, This Study will consider offering the same cleaning service during the fall hunting season, although it is possible that turkey hunters may not wish to surrender tissue samples from their catches because of the smaller size. In this event, this Study will consider a swap of domestic turkey for wild turkey (perhaps with some monetary compensation) or collecting turkey directly as was done in the initial game study. Before dressing, turkeys will be weighed to the nearest gram and examined for sex classification. Sex will be determined by examining the breast feathers of the turkeys. (The feathers of the hen are rounded and buff colored while the feathers of the gobbler are squamate and black-tipped.) Sex of the turkeys may also be determined by the relatively greater height of the gobbler and the presence or absence of a beard or spur. Weight and sex of the turkeys will be recorded in the appropriate field laboratory notebook. All turkeys will be dressed according to standard hunting practices, and edible portions of the muscle tissue will be removed from various points on the body. The exterior of all tissues harvested will be rinsed with distilled water to remove foreign debris and blood. In the case of each turkey, approximately 700 g of white meat will be removed from the breast, and approximately 300 g of dark meat will be removed from the legs. All muscle samples

will be weighed and cut into approximately 1" cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and muscle tissue will be transferred into a pre-labeled, chemically clean, 1000-mL I-Chem jar. A duplicate set of samples will be collected and retained for possible evaluation of cooking loss. All of the muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU). At the URCF, samples will be stored at -20^{o} C where a subset will be homogenized. Once homogenized, the samples will be separated into six aliquots and transferred into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived at the URCF. Splits will be made available to MDEQ parties upon request. The remainder of each turkey carcass will be placed in a plastic bag and stored frozen until the end of the study.

For rabbits (or other small game) that have no specific hunting season, this Study will collect the samples from the sampling locations specified through hunting (or trapping) as was done in the initial game study. Before dressing, rabbit specimens will be weighed to the nearest gram and examined for sex classification. Sex in rabbits will be determined by examining external sex organs and urethral openings. (Males have a rounded, protruding penile sheath with a rounded urethral opening; females have an elongated vulva with a slit opening.) Weight and sex of the rabbits will be recorded in the appropriate field laboratory notebook. Rabbits will be dressed (*i.e.*, cleaned and skinned) according to standard hunting practices, and all edible portions of the muscle tissue will be removed from various points on the body. The exterior of all tissues harvested will be rinsed with distilled water to remove foreign debris, fur, etc. Muscle samples from the carcass will be weighed and cut into approximately 1" cubes and then placed in pre-labeled, chemically clean I-CHEM jars (500 or 1000-mL). A duplicate set of samples will be collected and retained for possible evaluation of cooking loss. All of the muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At the URCF, samples will be stored at -20^{o}C where a subset will be homogenized. Once homogenized, the samples will be separated into four aliquots and transferred into four chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived at the URCF. Splits will be made available to MDEQ upon request. The remainder of each rabbit and/or squirrel carcass will be placed in a plastic bag and stored frozen until the end of the study.

3.0 SAMPLE COLLECTION AND INITIAL PREPARATION

The primary purpose of this sampling is to collect sufficient tissue from the edible portions of select game species prepared in a manner relevant to human consumption that can be used to determine the concentration of congener-specific PCDD/Fs and lipids. Sufficient muscle and select organ tissues (deer only) will be retained to analyze separately if needed or to conduct studies on the effects of cooking on the loss of PCDD/Fs. Game will be collected within various areas along the Tittabawassee River and will be harvested just prior to and during the hunting season, so that the sampling effort will represent normal hunting activities. The appropriate MDNR, MDEQ, and USFWS offices will be contacted well prior to any sampling activity to fulfill any permitting requirements. MDNR, MDEQ and USFWS will be notified of sampling dates and locations prior to actual sampling.

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and are described in the Health and Safety Plan developed by ENTRIX (2003) for the original game sampling study. Use and possession of firearms must be in accordance with all Federal, State, and local laws and regulations. Firearms shall not have a cartridge in the chamber while in a motor vehicle. Firearms left or stored in unattended vehicles must be placed out of public sight and the vehicle locked. Firearms will not be worn, carried, or used in an irresponsible, unsafe, or unprofessional manner. Firearms will not be used if they present a danger to life or property or if a problem with public relations may result. Each employee, regardless of employment status, and official volunteers required or requested to use firearms in conduct of official duties will be provided safety and handling training or must provide verifiable documentation of equivalent training. Examples of acceptable training would be informal field and/or classroom training conducted by appropriate personnel knowledgeable in firearm safety, self-instructed video training, formal classroom training from firearms professionals, or a combination of each.

Sample collection activities will be initiated only after the game sampling work plan is approved by MDEQ, and permit requirements are met. This section details the overall sampling methodology, equipment and techniques to be employed in the game sampling effort, considerations for ensuring preservation of sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation, and shipping. The method of take will include standard firearm hunting practices (primarily shotgun and short-range center-fire rifle) or possibly live-trapping in the case of small game. In addition, the use of firearms and spotting lights may be employed if necessary for white-tailed deer and wild turkey. All practices will be conducted in such a way to maximize public safety.

For each game animal harvested, the following field observations and measurements will be recorded:

- Sample ID
- Species
- Gender
- General site description
- Photographs
- GPS coordinates
- Date and time of harvest
- Collectors initials

After recording observations and measurements, the sample will be processed as described below.

3.1 Sampling Equipment and Use

The project team will assemble and pack all equipment specified below in advance of the sampling event. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

The field equipment and supplies needed for game sample collection may include:

- SOP for game sampling
- Site Health and Safety Plan
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Detailed maps of sampling site locations
- Pencils/Pens
- Sharpie waterproof markers
- Waterproof field notebook and clipboard
- Field Sampling Checklist
- Chain of custody (COC) forms
- Field data documentation forms
- Sample labels and sample tags
- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- Collecting permits
- 2-way radio and/or cell phone
- GPS receiver
- Digital camera
- Appropriate field clothing (hunter orange if hunting during daylight hours)
- Headlamps
- Spotlights

- Duct tape
- Garbage bags
- Packing tape
- Freezer tape
- String
- Field thermometer
- Appropriate firearms
- Plastic sheeting
- Several sizes of plastic bags for holding individual samples
- Large plastic Ziploc bags
- Aluminum foil (extra heavy duty)
- Gloves
- Holding trays
- Sawzall electric saw
- Automatic turkey plucker
- Hunting knives
- Knife sharpener
- Absorbent pads
- Masks
- Goggles
- Disposable lab coats
- Rain gear
- Coolers
- Ice (wet ice, blue ice packets, or dry ice)
- Filament-reinforced tape to seal ice chests for transport to the central processing laboratory
- Sample preservation and shipping supplies
- Tape measure
- Agent grade acetone and hexane
- Chemically clean glass I-CHEM jars (1000, 500, 250 ml capacity)
- Top loading balance
- Mops and Bleach
- Rope/Gambrel/Hoister

3.2 Sample Location and Timing

Game sampling will occur within the Tittabawassee River Study Area, including the Shiawassee National Forest. Four collection sites will be selected, all located downstream of Midland, MI. One reference site will be located upstream of Midland, MI for new species such as rabbits that were not harvested in the first wild game study or to supplement data on other species as needed. The location (*i.e.*, latitude and longitude) of each sampling location will be recorded on each field data sheet. If a Global Positioning System unit is used to provide location information, the accuracy or design

confidence of the unit will be noted. White-tailed deer, wild turkey, and cottontail rabbits (or alternate small game) will be sampled from mid to late November. In order to easily locate and harvest the deer in adequate numbers, some sampling may occur at night with the use of spotlights and bait stations.

3.3 Sampling Procedure

This section details the overall sampling methodology, equipment, and techniques to be employed in the game sampling.

3.3.1 Deer

A. White-tailed deer will be collected by standard hunting practices during the fall hunt and in compliance with state hunting regulations. Hunters will use firearms to harvest deer. If study personnel perform the harvest, they will likewise use standard hunting practices and comply with state collecting permits.

B. If hunter-harvested deer are used, the hunter will bring the harvested deer to the preparation area for sample collection. The sampling team will record the location from which each deer was harvested based on the hunter's information. Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

If study personnel collect the deer, an "all-clear" message will be communicated to the field team after the harvest is done, the location of each harvested deer will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimen and weight, size, and gender recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time, and collector initials.

E. The deer carcass will be field dressed according to standard hunting practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane before each deer is dressed.

F. Specific organs will be removed, weighed and then rinsed with distilled water to remove any foreign debris and/or fur that may have come into contact with the tissue during field dressing. These include liver, kidney, heart, and brain. Additionally, deer fat from the hide will be removed. Approximately 1000 g of each tissue will be retained and cut into approximately 1-inch cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled.

G. After skinning, edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area, and similarly rinsed with distilled water to remove foreign debris or dirt that may have come into contact with the tissue during field dressing. Each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close a possible. A duplicate set of muscle samples from the same areas will be collected and preserved for possible studies of cooking loss.

H. The actual weights for each muscle/meat group will be recorded in the appropriate field notebook and then transferred into a single chemically clean, 1000-mL I-Chem jar.

I. Deer muscle and organ tissue samples in I-CHEM jars will be immediately placed on ice.

J. Mops and bleach solution will be used to clean dressing areas following daily activities.

K. Any deer carcasses remaining from animal harvested for this Study (not supplied by hunters) will be held frozen at $-20^{o}C$ until the end of the study and disposed of in accordance with state and local regulations.

3.3.2 Turkey

A. Wild turkey will be collected by standard hunting practices or in compliance with state collecting permits. Authorized personnel will use appropriate firearms to harvest turkey.

B. After a harvesting period is complete and an "all-clear" message has been communicated to the field team, the location of each harvested turkey will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Turkeys will be tagged with pre-printed sample labels. One sample label will be attached to a limb of the turkey and one sample label will be attached to the bag in which the turkey carcass is placed.

D. Digital photographs will be taken of the specimen and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time and collector initials.

F. After placing the turkey carcass in the appropriate collection bag, the animal will be transported to a nearby field dressing station.

G. Before dressing, turkeys will be weighed to the nearest ounce and examined for sex classification. Sex will be determined by examining the breast feathers of the turkeys. (The feathers of the hen are rounded and buff colored while the feathers of the gobbler are squamate and black-tipped.) Sex of the turkeys may also be determined by the relatively greater height of the gobbler and the presence or absence of a beard or spur.

H. Weight and sex of the turkeys will be recorded in the appropriate field laboratory notebook.

I. Turkeys will be dressed according to standard hunting practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone or hexane before the turkey is dressed. An automatic turkey plucker will be used to remove the feathers from the turkeys.

J. Edible portions of the muscle tissue will be removed from the turkey, and rinsed with distilled water to remove any foreign debris that might have contacted the tissue during dressing. Specifically, muscle tissue will be removed from the chest and leg regions of the turkey. Approximately 700g of white meat will be removed from the breast, and approximately 300 g of dark meat will be removed from the legs. A duplicate set of muscle samples from the same areas will be collected and preserved for possible studies of cooking loss.

K. All muscle samples will be cut into approximately 1-inch cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is recorded and then transferred into a single chemically clean, 1000-mL I-Chem jar.

L. Turkey muscle samples in I-CHEM jars will be immediately placed on ice.

M. The remainder of each carcass will be placed in a plastic bag, stored frozen at $-20^{o}C$ until the end of the study, and disposed of in accordance with state and local regulations.

3.3.3 Rabbit

A. Rabbits or alternate small game species will be collected by standard hunting practices or in compliance with state collecting permits. Authorized personnel will use appropriate firearms to harvest rabbits. Live trapping will be considered as well.

B. After a harvesting period is complete and an “all-clear” message has been communicated to the field team, the location of each harvested rabbit will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Rabbits will be tagged with pre-printed labels. One sample label will be attached to a hind limb of the rabbit and one sample label will be attached to the bag in which the rabbit carcass is placed.

D. Digital photographs will be taken of the specimen and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, date, time, and collector initials.

F. After placing the rabbit carcass in the appropriate collection bag, the animal will be loaded onto a field vehicle for transport to a nearby field dressing station.

G. Before dressing, rabbit specimens will be weighed to the nearest ounce and examined for sex classification. Sex will be determined by examining external sex organs and urethral openings. (Males have a rounded, protruding penile sheath with a rounded urethral opening; females have an elongated vulva with a slit opening.)

H. Weight and sex of the rabbits and/or squirrels will be recorded in the appropriate field laboratory notebook.

I. Rabbits will be dressed according to standard hunting practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone or hexane before each rabbit is dressed.

J. All edible portions of the muscle tissue will be removed from each rabbit. Specifically, muscle tissue will be removed from the legs and torso of collected specimens. The collective muscle tissue weight will be recorded in the field notebook. A duplicate set of muscle samples from the rabbit (or rabbits collected in the same vicinity) will be collected and preserved for possible studies of cooking loss.

K. All muscle samples will be cut into approximately 1-inch cubes and then placed in pre-labeled, chemically clean I-CHEM jars (500 or 1000 ml capacity).

L. Muscle samples in I-CHEM jars will be immediately placed on ice.

M. The remainder of each carcass will be placed in a plastic bag, stored frozen at $-20^{o}C$ until the end of the study, and will be disposed of in accordance with state and local regulations.

3.4 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is preserved by prevention of loss

of contaminants already present in the tissues and prevention of extraneous tissue contamination.

All potential sources of contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. Ice chests will be scrubbed clean with detergent and rinsed with distilled water after each use to prevent contamination. To avoid contamination from melting ice, samples will be placed in waterproof plastic bags. Sampling equipment that has obviously been contaminated will be cleaned or not be used. All utensils or equipment that will be used directly in handling game will be cleaned prior to each sampling trip, rinsed in acetone and pesticide-grade hexane, and stored in aluminum foil until used. Between sampling sites, the field collection team will clean the preparation surfaces by rinsing them with acetone and hexane and mopping with bleach at the end of the sampling period or as necessary.

Ideally, all sample processing of collected game will be performed at a sample processing facility under clean room conditions to reduce the possibility of sample contamination. If sample preparation must be performed in the field, a clean area will be set up away from sources of contamination to help reduce the potential for inadvertent surface and airborne contamination of the samples. Use of a mobile laboratory or use of a portable resection table and enclosed hood would provide the best environment for sample processing in the field. If sample processing is conducted in the field, a notation will be made in the field records and on the sample processing record.

3.5 Field Recordkeeping

Thorough documentation of all field sample collection and processing activities is necessary for proper interpretation of field survey results. The data collection phase includes the completion of a various sample-tracking forms, which includes information regarding the sample collection procedures. The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel will be properly trained in these areas and perform these tasks in secured access facilities.

Field personnel will document all sampling activities in accordance with the Work Plan and sample specific SOPs. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing laboratory. These are 1) Field record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection and (b) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

3.5.1 Field Record Form

For each individual game animal that is collected, the following observations and measurements will be recorded at a minimum:

- Species
- Date and time collected
- Temperature and weather conditions
- Site location and GPS coordinates
- Sex, approximate weight, and size
- Type of all tissues collected
  - Rump roast, tenderloin, and backstrap meat for deer
  - Liver, heart, brain, or fat for deer
  - Breast and leg meat for turkey
  - All muscle tissue for rabbit or small game
- Weight of all tissue collected
- Collectors name(s) and signatures
- Affiliation (including telephone number and address)

3.5.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format. The QA/QC samples will be labeled accordingly.

Each sample label will have a unique sample identification number consisting of: a two-letter prefix to distinguish the project ID, a 2-digit number to distinguish location, a two-letter abbreviation for the animal species, and a 2-digit number to designate animal number. In addition, tissue samples will be labeled ‘L’ or ‘M’ for liver or muscle, accordingly. Field and laboratory blanks will be labeled with the project ID, date, and type of blank that are being collected. Example ID labeling schemes are illustrated below.

Example Game Sample ID Labels

TR01DR01
TR = Tittabawassee River Project
01 = Location Reference
DR = Deer; **TY** = Turkey; **RT** = Rabbit; **SL** = Squirrel
01 = Animal number

TR01DR01L1
TR = Tittabawassee River Project
01 = Location Reference
DR = Deer; **TY** = Turkey; **RT** = Rabbit; **SL** = Squirrel
01 = Animal number
L, H, B, F, M = Liver, Heart, Brain, Fat, or Muscle tissue
1,2,3… = Replicate tissue sample number

TRMMDDBAB01
TR = Tittabawassee River Project
MMDD = Date (Month and Day only)
BAB = Blank sample type

- BAB = Butchering Atmospheric Blank
- BSR = Butchering Start Rinsate
- BER = Butchering End Rinsate
- HAB= Homogenate Atmospheric Blank
- HSR = Homogenate Start Rinsate
- HER = Homogenate End Rinsate

01 = Replicate number

A completed sample identification label will be taped to each container and the individual specimen will be placed in a waterproof plastic bag.

3.5.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual game specimen. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling date/time
- Processing and analysis requested
- Preservation method (wet/dry ice)

After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual sample. Information on the COC label will also be recorded on the COC form.

3.5.4 Chain-of-Custody Form

Game samples collected for analysis will be tracked in the field and in transit to the processing laboratory and then to the analytical laboratory. Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g*., ice chest) used. All pertinent information will be entered into the chain-of-custody form in the field including in-transit and laboratory delivery relinquishment/receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for tissue samples; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight, or in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

3.5.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, weather conditions, equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the game sample data. This will also include method of harvest, start time, ending time, sampling duration, sampling location, and sampling conditions.

3.6 Sample Handling

3.6.1 Initial Field Preparation and Sorting

Tissue from the selected target species will be rinsed in distilled water to remove any foreign material or blood from the external surface. Equipment used in processing samples for organics analysis will be of stainless steel, anodized aluminum, borosilicate

glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Tissue sampling will be done on glass or PTFE cutting boards that are cleaned properly between samples or on cutting boards covered with heavy-duty aluminum foil that is changed after each sample preparation. Tissue will be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles. Samples will be stored in sealed glass containers as noted.

Prior to preparing each sample, utensils and containers will be washed with detergent solution, rinsed with tap water, soaked in reagent-grade hexane or acetone, and rinsed with nanopure water. Work surfaces will be cleaned with reagent-grade hexane or acetone, washed with distilled water, and allowed to dry completely. Knives, measurement boards, etc., will be cleaned with reagent-grade hexane or acetone followed by a rinse with contaminant-free distilled water between each game sample.

All game samples will be stored in pre-cleaned containers that are of sufficient size for sample content. All sample jars used are ordered as pre-cleaned and QA/QC grade. If jars are not pre-cleaned and QA/QC grade, then they will be reagent grade acetone and hexane rinsed before use. After the jars have been dried they will be sealed and stored until needed.

3.6.2 Length or Weight Measurements

Each individual game species will be measured to determine total body length and weight matched to the desired size class, and the information recorded on the appropriate forms.

3.6.3 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PCDD/PCDF congeners as if it were an actual sample. Field blanks will be submitted at a rate of five percent of the total number of samples to conform with US EPA's recommendations. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for game samples will consist of muscle homogenates from game species collected spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8- TCDF. MS/MSD analyses of homogenates from other deer tissue samples (*i.e.*, liver, heart, etc.) will be performed if these tissues are included in the analyses.

3.7 Sample Packaging

After sample processing, each sample will be individually stored in chemically clean glass containers. The sample identification label will be taped to the outside of each container, each container will be placed into a waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual samples for the same species from the sample location will be kept together (if possible) in one large waterproof plastic bag in the same shipping container

(ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

3.8 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed. Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours. If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer unit will be used for temporary storage of game samples and remaining tissue at the field dressing location. Long-term storage of additional tissue or samples (until study termination) will take place at a storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University where they will be stored at –20°C until homogenization. All samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified.

3.9 Sample Shipping to Processing Facility

The tissue samples will be hand-delivered or shipped to the processing location as soon as possible after collection and initial field processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples will be transported within 48 hours for processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag

or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

4.0 FINAL SAMPLE PREPARATION AND SHIPPING

4.1 Sample Receipt and Chain-of-Custody

Game samples will be shipped or hand-carried from the field and delivered to a processing location for further sample processing. Sample processing and distribution for analysis ideally will be performed by one processing location. Transportation of samples from the field will be coordinated between the sampling team supervisor and the supervisor responsible for sample processing and distribution. An accurate written custody record will be maintained so that possession and treatment of each sample can be traced from the time of collection through analysis and final disposition.

Game samples will be brought (or shipped) to the sample processing location in sealed containers accompanied by a copy of the sample request form, a chain-of-custody form, and the field records. Each time custody of a sample or set of samples is transferred; the Personnel Custody Record of the COC form will be completed and signed by both parties. Corrections to the COC form will be made in indelible ink by drawing a single line through the original entry, entering the correct information and the reason for the change, and initialing and dating the correction. The original entry should never be obscured.

When custody is transferred from the field to the sample processing location, the following procedure will be used:

• Shipping time will be noted (has the shipping time exceeded the appropriate time for preservation method used?).
• Check that each shipping container has arrived undamaged and that the seals are intact.
• Open each shipping container and remove the copy of the sample request form, the COC form, and the field records.
• Note the general condition of the shipping container (samples iced properly with no leaks, etc.) and the accompanying documentation (dry, legible, etc.).
• Locate individual samples listed on the COC form and note the condition of their packaging. Individual specimens should be properly wrapped and labeled. Note any problems (container broken, illegible labels, etc.) on the COC form.
• If individual samples are packaged together, check the contents of each composite sample container against the field record for that sample to ensure that the individual specimens are properly packed and labeled. Note any discrepancies or missing information on the COC form.
• Initial the COC form and record the date and time of sample receipt.
• Enter the following information for each composite sample into a permanent laboratory record book and, if applicable, a computerized database:

1 Sample identification number (specify conventions for specimen number)
2 Receipt date (YYYYMMDD)
3 Sampling date (YYYYMMDD)

4 Sampling site (name and/or identification number)
5 Game species (scientific name or code number)
6 Weight of sample

• If samples have been shipped on wet or blue ice, distribute them immediately to the technician responsible for sample preparation. If samples have been shipped on dry ice, they may be distributed immediately to the technician for processing or stored in a freezer at -20^{o} C for later processing. Once processed, samples should be stored according to the procedures described below.

4.2 Sample Processing

A. Tissue samples received by the processing location will be stored at –20°C until they are ready for homogenization. Replicate samples or samples not immediately needed for sampling will be stored under the same conditions.

B. To ensure even distribution of contaminants throughout tissue samples and to facilitate extraction and digestion of samples, the sample will be ground and homogenized prior to being sent to the analytical laboratory for analysis. Previously cubed game samples will be ground and homogenized in stainless steel blenders. Grinding and homogenization of tissue may be easier when it is partially frozen. Chilling the grinder/blender briefly with a few chips of dry ice may also help keep the tissue from sticking to it. The game sample will be ground until it appears to be homogeneous. The ground sample should then be divided into quarters, opposite quarters mixed together by hand, and the two halves mixed together. The grinding, quartering, and hand-mixing steps should be repeated at least two more times. If chunks of tissue are present at this point, the grinding and homogenization will be repeated. The preparation of each individual homogenate will be noted on the sample processing record. At this time, individual homogenates may be frozen separately. The sample processing location will prepare aliquots of the individual homogenates for analysis, distribute the aliquots to the appropriate laboratory, and archive the remainder of each homogenate along with the remaining tissue. Before, during, and after sample preparation, blenders will be washed with Liquinox soap, rinsed three times with distilled water, and reagent grade acetone and hexane rinsed. Other equipment and surfaces that may potentially contact the sample will be likewise cleaned regularly. Verification of the efficacy of cleaning procedures may be documented through the analysis of processing blanks or rinsates.

C. Homogenates will be aliquoted into four to six separate chemically clean I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Sample IDs will be labeled for each replicate homogenate sample as described above.

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

The actual sample size required will depend on the analytical method used and the laboratory performing the analysis. Therefore, the exact sample size required for each type of analysis will be determined in advance with the analytical laboratory selected. The frozen aliquot(s) will be transferred on dry ice to the analytical laboratory accompanied by a sample transfer record. The sample transfer record will include a section that serves as the analytical laboratory COC record. The COC record will be signed each time the samples change hands for preparation and analysis.

Care will be taken during sample processing to avoid contaminating samples. This may be particularly problematic for PCDD/Fs, given the low levels that are of potential concern. Potential sources of contamination include dust, instruments, utensils, work surfaces, and containers that may contact the samples. All sample processing will be done in an appropriate laboratory facility under clean room conditions. Clean rooms or work areas will be free of organic contaminants. Periodic wipe tests may be conducted in clean areas to verify the absence of significant levels of organic contaminants. All instruments, work surfaces, and containers used to process samples will be of materials that can be cleaned easily.

4.3 Sample Shipping to Analytical Laboratory

Tissue homogenates, field blanks, and MS/MSD samples will be packaged and shipped for laboratory analysis according to US EPA/REAC guidelines (US EPA, 1994) as noted above.

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples will be transported to the analytical laboratory as soon as feasible after processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure

the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the analytical laboratory unless prior plans for such a delivery have been agreed upon with the laboratory staff. The time the samples were collected and time of their arrival at the analytical laboratory will be recorded on the COC form.

4.4 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD/F detected across sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, date and time of sample collection, sample and tissue type, lipid content of tissues, PCDD/F concentrations of tissues, and treatment of LODs for non-detects. The data entry will be verified to ensure the accuracy of the information. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

4.5 Data Analysis

The objective of data analysis is to identify and report the PCDD/F concentrations measured in game species that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error), and develop a valid PDF for use in exposure and risk assessment. These steps will be outlined in the Exposure Assessment Work Plan currently under development for submission on December 1, 2006. Ultimately, this information will be used to calculate the potential risk of PCDD/F exposure to humans.

5.0 References

Blasland, Bouck & Lee. 1999. Sampling and Analysis Plan/Data Collection and Analysis Quality Assurance Plan. Blasland, Bouck & Lee, Inc., Syracuse, NY.

ENTRIX, 2003. Draft Work Plan For The Interim Response Activity of Evaluating Wild Game Taken From The Tittabawassee River Floodplain. ENTRIX, Inc. East Lansing, Michigan.

US EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - US EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

Domestic Livestock Study Plan

Study Objectives

1. To identify those locations along the Tittabawassee River where livestock is raised, identify the types of livestock raised and how it is used for consumption,
2. To identify and collect an adequate number of samples of local livestock (*i.e.*, chicken, chicken eggs, cow's milk, beef, and pork) most commonly raised and consumed by local residents from agricultural properties along the Tittabawassee River,
3. In the absence of any locally grown livestock, to discuss alternate means to gather such information for purposes of risk assessment,
4. To identify and prepare individual edible portions of various locally-raised livestock for analysis in the same manner as is commonly done by consumers, and
5. To submit those livestock tissue samples to a qualified laboratory for analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) relevant to soils along the Tittabawassee River.

This Study will preserve tissue from the livestock sampling in the event that additional or confirmatory sampling is required. The analytical results from the livestock tissue sampling will serve as the concentration term in the development of the probability density function (PDF) used to estimate PCDD/F exposure through ingestion of various livestock or animal products. The necessary data inputs, methods and decisions used to create this specific PDF will be detailed in the Exposure Assessment Work Plan currently under development. Other aspects of PCDD/F exposure through livestock or animal product ingestion, such as weighting the use of homegrown livestock or animal products to supplement the diet, rate and frequency of consumption of specific livestock or animal products, and accounting for preparation or cooking loss of PCDD/Fs will also be detailed in the Exposure Assessment Work Plan currently under development.

The sampling plan and methods for acquiring qualitative and quantitative data on homegrown livestock consumption by residents along the Tittabawassee River will be developed primarily from the planned Activity Survey and other sources of information such as the University of Michigan Dioxin Exposure Survey (UMDES) questionnaire information, local ordinances, or information gathered from the MDA, local extension agents, or other local sources of information developed to fill relevant data gaps that are identified. Any suggested modifications to this plan in terms of species, numbers, and preparation methods based on such information or suggestions, if relevant, will be adopted in order to improve the relevance and site-specificity of the livestock sampling protocol, thereby further reducing uncertainty. Planning and documentation of the sampling procedures will be done to ensure that collection activities are time and labor-effective and that sample integrity is preserved. It is anticipated that both collection and analysis of readily available livestock tissue can be completed within 12 months following approval of this work plan by MDEQ. If an alternate method must be used to develop such information, it may require additional time for PCDD/F body burdens to

reach steady state or to account for the normal rearing of livestock prior to slaughter. This will increase the amount of time needed to complete this Study.

1.0 Introduction

Soils along the Tittabawassee River have reported concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) that exceed current state generic criteria. Some of these soils are used for agricultural purposes currently and some rural residents may supplement their diet with homegrown livestock and animal products (*i.e.*, chicken and eggs, beef and dairy cattle, hogs, etc.). Past investigation by the Michigan Department of Environmental Quality (MDEQ) has reported that chicken eggs (n = 4) collected from property along the river contained PCDD/Fs at levels that might be of concern if such foods comprised a significant amount of the diet. This small sample size, limited to eggs, and uncertainty over potential human exposure to these and other sources of homegrown animal products makes it difficult to draw firm conclusions about the actual human health risks posed by potential consumption of livestock raised along the river. Nonetheless, since rural residents, their families, and others may consume livestock raised along the Tittabawassee River, ingestion of livestock constitutes a potentially completed exposure pathway and requires evaluation and inclusion in the Human Health Risk Assessment (HHRA).

Since the existent data are judged inadequate for risk assessment purposes based on limited numbers of samples for livestock, This Study proposes to carry a two-phased approach to assessing livestock and related foodstuff exposure pathways along the river. An Activity Survey will ascertain the current presence of livestock reared for consumption along the river. The extent of homegrown livestock consumption, frequency and duration of ingestion, and preparation methods will also be addressed in the Activity Survey. Interviews with local farmers or rural residents, participants at Farmers Markets, expertise provided by the Michigan State Agricultural Extension Services, and the Michigan Department of Agriculture (MDA) will supplement this information. Based on these results, This Study will collect relevant livestock tissue samples for analysis based on livestock raised locally for consumption (*i.e.*, chicken, chicken eggs, cow's milk, beef, and pork). The edible portion of these samples will be prepared in the manner most common to these foods, and submitted for analysis. Sufficient tissue would be retained to conduct studies of cooking loss or additional analyses if required.

It should be noted that it is possible that no one will be identified that raises or consumes locally raised livestock from along the river either because it is uncommon or non-existent. In such a case, Dow representatives will confer with MDEQ on alternatives.

2.0 SAMPLING DESIGN FOR COLLECTING LIVESTOCK AND ANIMAL PRODUCTS CONCENTRATION DATA

Development of the final livestock-sampling plan that is site-specific, reasonable, and relevant will be derived from input from the planned Activity Survey, results from the UMDES survey, experts from MDA, local county extension agents, local farmers, and rural residents. In addition to collecting tissue from the relevant livestock species or animal products, the study protocol provides recommendations on sample preparation so that the HHRA can be based on actual amounts of PCDD/Fs in livestock or animal products consumed by residents.

There are six major parameters that will be specified prior to the initiation of the field collection activities:

- Site selection
- Target species or product
- Target analytes (PCDD/Fs)
- Target analyte screening values
- Sampling times
- Sample type

These parameters will be documented on a sample form prepared for each sampling location found along the Tittabawassee River. The sample form will provide the sampling team with readily available information on the study objective, site location, site name/number, target tissue or product to be collected, number of individual animals to be collected, sampling and preparation method to be used, target analytes (PCDD/Fs) to be evaluated, sampling date, and number of replicates to be collected. The sampling manager will retain the original sample forms and a copy kept with the field logbook.

2.1 Site Selection

Sampling sites for livestock along the Tittabawassee River will be selected based on the existence of livestock used for human consumption identified from the Activity Survey or through observation or from information provided by local residents. The potential locations can be refined based on local ordinances and regulations that might preclude the raising of livestock. The final areas for consideration may include locations where soil contamination exists, and where livestock are or could be raised under local ordinances. Modification of initial site selection may occur upon interview results or recommendation of local experts as necessary.

The procedures required to identify livestock sampling sites will be straightforward. All sampling will be conducted downstream of Midland, and in areas where food animals can be raised by ordinance and regulation. Additional locations will be chosen based on responses to the Activity Survey as well as information gathered by the UMDES or provided by MDA and local agricultural experts. Soil sampling points near each livestock sampling location will be identified and the results reviewed to examine the

possibility of correlating contaminant concentrations between different environmental media (*i.e.*, soil and livestock or animal products). If no soil or sediment sampling points exist in or near the livestock sampling location, additional soil or sediment samples will be collected for comparison. A reference sample or samples upstream of Midland may be selected for comparison or the residue content of store-bought meat, eggs, or dairy products may be determined from the literature for comparison.

The final selection of both the number and location of livestock or animal product samples will be based on information about the type and numbers of livestock raised, specific properties where they are raised, willingness to cooperate with the study among animal owners, timing of slaughter for muscle or other tissue samples, and consumption patterns among residents. Once the various sampling sites have been selected, they will be plotted and numbered on the existing Geographic Information System (GIS) using a Global Positioning System (GPS). It is conceivable that no properties where livestock or animal products can be sampled will be found either because they are very rare or non-existent in the floodplain or access is denied. In such a case, Dow representatives will discuss with the MDEQ alternative methods that could be used to assess this route of exposure.

2.2 Target Livestock and Animal Product Selection

The livestock and animal products selected for this site-specific study are those most common to the diet: domestic chickens and chicken eggs, domestic beef cattle and cow's milk, and domestic pigs. Cattle, pigs, and chickens are herbivores or omnivores and their diet and behavior makes them potentially good indicators of exposure conditions to the soils along the river.

The final selection of target species will be determined based the information derived from the Activity Survey as well as identification of the primary livestock or animal products raised and consumed from the UMDES questionnaire or from other local sources that can be independently verified. It is anticipated that the primary focus of the livestock sampling will be on those species named above although other species may be included or substituted in the data collection process if they are raised locally.

In the event that five properties cannot be located or access is denied, Dow representatives will discuss with the MDEQ alternate methods and approaches to acquire these data. In general, muscle tissue will be collected following slaughter of livestock in sufficient amounts to allow retention of tissue for any additional analysis needed. In the case of cattle, certain other tissues or organ meats (*i.e.*, liver) will also be collected for possible analysis if such tissues are utilized by specific segments of the population. In terms of chicken eggs and cow's milk, several composites of these animal products will be collected from each individual location over time to estimate the exposure through consumption. A preliminary list of species, animal products, and number of samples per species/product are shown in the following table.

Table 1. Livestock/Animal Product Sampling Plan by Species/Product

Target Species	Location	Sample type	# Tissue Samples/Location	Total # of Samples
Cattle	5	Muscle, organs	1 - 2	5 - 10
Pig	5	Muscle	1 - 2	5 - 10
Chicken	5	Muscle	5 - 10	25 - 50
Chicken eggs	5	Egg composite	5 - 10	25 - 50
Cow's milk	5	Milk composite	5 - 10	25 - 50

Other species and number or type of samples may be added or changed based on the site-specific Activity Survey, the UMDES information, input from local residents, or MDA and local agricultural experts.

2.3 Target Analyte Selection

At present, the primary focus of this sampling effort is to determine the concentrations, patterns, and variability of polychlorinated dioxins and furans (PCDD/Fs) in various livestock or animal product tissue collected from along the Tittabawassee River. Other persistent pollutants (*i.e.*, PCBs, chlorinated pesticides, metals, etc.) commonly or previously found in livestock muscle or organ tissue or animal products may be included in the analysis to provide context and additional information.

2.4 Target Analyte Detection Limits

The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of the PCDD/Fs in select tissue samples from livestock or animal products collected from selected locations along the Tittabawassee River. In the case of congener-specific PCDD/Fs analyses, the detection limit selected is generally in the range of 0.1 part per trillion (ppt) in view of the amount of tissue available for analysis (results to be reported on a wet weight and lipid-adjusted basis). Non-detects will be handled as Limit of Detection (LOD) = 0.

2.5 Sampling Times

Sampling will be conducted during the period when the various livestock species or animal products are most frequently harvested. For chicken eggs and cow's milk that may be collected daily, sampling will be conducted at weekly intervals once it is certain that the dairy cattle and chickens have been on site long enough to have developed a steady state body burden of the PCDD/Fs. For meat animals, the sampling will occur at the planned slaughter for privately owned animals or once the animals have again reached steady state in terms of body burden (except in the case where normal slaughter takes place before achieving a steady state body burden). Therefore, this sampling activity should coincide with the normal and expected harvesting of edible portions of existent privately owned livestock or animal products by residents along the Tittabawassee River during the latter part of 2006. The sampling locations will be re-visited to observe animal health and husbandry conditions until the targeted sample size

or normal harvest for each species is reached. Possible exceptions to the recommended sampling periods for different livestock species or animal products will be determined by information gathered by the Activity Survey, the UMDES questionnaire or other sources of site-specific information, or input from MDA and local residents that suggest alternative sampling periods should be used. Therefore, the entire sampling effort will be dependent on the presence or abundance of the target livestock species or animal products along the river, identification and access of sampling locations, selection of appropriate sampling periods for composite (eggs and milk) or whole animal sampling, and that the animals have lived on the site long enough to accumulate a steady state body burden of PCDD/Fs, or in accordance with normal animal husbandry practices for that species. The actual sampling for each livestock species or animal products and the rationale for the sampling selection will be documented fully and the final report will include a description of sampling results.

2.6 Sample Type and Preparation

Individual or composite samples of edible muscle, organ tissue, or animal product will be obtained and analyzed based on the target species selected. The sampling objectives and approach are dependent on the targeted species.

For cattle and pigs, the objective will be to harvest a representative sample of beef and pork that is consumed by residents that raise cattle and pigs along the Tittabawassee River. Relative to age, this Study will try to harvest a similar age structure of privately owned cattle between identified locations. However, it may not be possible to match all possible variables such as age, length of exposure, and gender based on the limited sample size. These factors will be evaluated once the beef and pork samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For chicken, the objective is also to collect a representative sample of primarily female chickens that would best represent typical consumption by residents raising these animals on selected locations. While cattle and pigs will provide sufficient tissue from a single animal for analysis, single chickens may not. It may be necessary to composite two or more chickens from the same location to provide sufficient tissue for analysis, duplicate samples, and studies of preparation and cooking loss. Again, the potential influences of variables such as age, length of exposure, and gender will be evaluated once the samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For chicken eggs and cow's milk, the sampling will be somewhat simpler since eggs and milk for analysis can be collected repeatedly once the animals have been established long enough for PCDD/F body burdens to be at steady state. Once at a steady state body burden, a sample collection will occur once a week for one month in each of the four seasons. In the event that there are multiple chickens or dairy cattle at a specific location, the eggs or milk collected at a specific sampling time may be composited for analysis or analyzed individually. The potential influences of variables such as age and length of exposure will be evaluated once the samples are analyzed and, if significant, the

differences will be factored into the development of weighting factors and the exposure PDFs.

The preparation of the samples from each livestock species or animal product collected will be done to reflect the general practice among consumers and will reflect as well the preparatory steps prior to cooking. In the case of beef and pork, trimmed skinless muscle meat should be used for assessing exposure to members of the general population since consumers of beef and pork do not eat the skin. Samples of chicken will be prepared with the skin on and skin off. Preparation methods for various livestock and animal products and other factors that might influence residues will be verified in the site-specific Activity Survey. The consumption or use of other tissues (*i.e.*, organ meats) by some segments of the population will also be determined in the site-specific Activity Survey. Analysis of organ meats will occur only if these tissues are consumed or used by the populations in question. A sufficient amount of tissue from each livestock species or animal product harvested will be retained for possible additional analysis if cooking loss needs to be ascertained or other analysis is required for purposes of ascertaining or refining exposure estimates.

Whole livestock animals identified as part of the sample will be harvested in accordance with the owner's need or because they have been on-site for a sufficient period of time based on attaining a steady state body burden as described above. These animals will be sorted by species, size, gender, and sample location in accordance with sample handling procedures detailed below. After samples have been collected and initial documentation has been completed, samples will be processed at a meat processing facility as is normally done to avoid contamination with soil. In this facility, livestock will be dressed according to standard practices. The following sections briefly discuss the processing procedures.

For cattle and pigs, it is intended to sample existing animal populations maintained by area residents, if possible. During the sampling period, the Study will locate these properties and owners and offer to pay for the butchering and purchase some meat and organ tissue from the animals at time of slaughter. Study representatives will be on hand at the time of slaughter both to oversee the process and collect the sample. For each cow or pig, the approximate size, weight, and age of the animal will be recorded. Certain tissues (*i.e.*, liver) will be removed as part of the dressing procedure and retained. At this stage, the exterior of all tissues harvested for purposes of analysis will be rinsed with distilled water to remove foreign debris, fur, etc., and placed in a clean, re-sealable plastic bag affixed with the appropriate labels. The samples will then be transported to an interim facility for further processing. At this facility and depending on the size of the tissues available, up to 1000 g will be cut into small cubes (approximately 1 cubic inch), weighed, and transferred into a chemically clean, 1 L I-CHEM jar.

Cattle and pig muscle tissue (approximately 5 pounds in total) will be collected after skinning and butchering. The edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area (other cuts of beef or pork may be substituted based on consumer preference following review of the Activity Survey or other sources of information). The exterior of all muscle harvested will again be rinsed

with distilled water to remove foreign debris, fur, blood, etc., and placed in a clean, re-sealable plastic bag affixed with the appropriate labels. The samples will then be transported to an interim facility for further processing. At this facility and depending on the size of the tissues available, each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and then transferred into a pre-labeled, chemically clean, 1000-mL I-Chem jar. A duplicate set of samples will be collected and retained for possible evaluation of cooking loss. All of the tissue and muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At this facility, samples will be stored at -20^{o}C where a subset will be homogenized. Once homogenized, the samples will be separated into six aliquots and transferred into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived. Splits will be made available to MDEQ upon request.

For chicken, this Study will purchase the chickens at the end of the egg collection period and process them in the following manner. Before dressing, chickens will be weighed to the nearest gram. It is anticipated that most of these chickens will be laying hens; however, weight and sex of the chickens will be recorded in the appropriate field laboratory notebook. All chickens will be dressed according to standard practices, and edible portions of the muscle tissue will be removed from various parts of the body. The exterior of all tissues harvested will be rinsed with distilled water to remove foreign debris and blood. The samples will then be transported to an interim facility for further processing. In the case of each chicken, approximately 350 g of white meat will be removed from the breast, and approximately 150 g of dark meat will be removed from the legs. All muscle samples will be weighed and cut into approximately 1" cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and muscle tissue will be transferred into a pre-labeled, chemically clean, 1000-mL I-Chem jar. A duplicate set of samples will be collected and retained for possible evaluation of preparation and cooking loss. In the event that a single chicken cannot provide sufficient tissue to meet analytical needs, two or more chickens from the same location will be composited to provide sufficient tissue weight. All of the muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At this facility, samples will be stored at -20^{o} C where a subset will be homogenized. Once homogenized, the samples will be separated into six aliquots and transferred into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived. Splits will be made available to MDEQ and other interested parties upon request. The remainder of each chicken carcass

or composited sample will be placed in a plastic bag and stored frozen until the end of the study.

For chicken eggs, this Study will collect the samples from the sampling locations specified once or twice a week for a month four times a year for a maximum of 10 eggs per week from a single location (maximum of 160 eggs/year/location). The egg samples from the weekly collections may be composited for analysis. Before compositing, eggs will be weighed to the nearest gram, and the weight and number of the eggs in the composite will be recorded in the appropriate field laboratory notebook. The exterior of eggs harvested will be rinsed with distilled water to remove foreign debris, etc. The eggs will be cracked and the contents placed in pre-labeled, chemically clean I-CHEM jars (500 or 1000-mL). A duplicate amount will be collected and retained for possible evaluation of cooking loss. All of the egg samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At this facility, samples will be stored at -20^{o}C where the samples will be homogenized. Once homogenized, the samples will be separated into four aliquots and transferred into four chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived. Splits will be made available to MDEQ and other interested parties upon request.

For cow's milk, this Study will collect milk samples from the sampling locations specified once or twice a week for a month four times a year for a maximum of 2 gallons per week from a single location (maximum of 32 gallons/year/location). The milk samples from the weekly collections may be composited for analysis if more than one cow furnishes milk from a single location. Milk samples will be weighed to the nearest gram, and the weight and number of cows furnishing the composite sample from each location will be recorded in the appropriate field laboratory notebook. The milk will be placed in pre-labeled, chemically clean I-CHEM jars (500-mL). A duplicate amount will be collected and retained for possible evaluation of processing loss. All of the milk samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At this facility, samples will be stored at -20^{o}C. The milk samples will be separated into four aliquots and transferred into four chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived. Splits will be made available to MDEQ upon request.

3.0 SAMPLE COLLECTION AND INITIAL PREPARATION

The primary purpose of this sampling is to collect sufficient tissue from the edible portions of select livestock species or animal products prepared in a manner relevant to human consumption that can be used to determine the concentration of congener-specific PCDD/Fs and lipids. Sufficient muscle and select organ tissues or egg and milk samples will be retained to analyze separately if needed or to conduct studies on the effects of cooking on the loss of PCDD/Fs. Livestock and animal products will be collected within various areas along the Tittabawassee River and will be harvested according to normal use or establishment of a steady state body burden, so that the sampling effort will represent normal consumption activities and exposure patterns. MDEQ will be notified of sampling dates and locations prior to actual sampling as requested.

Sample collection activities will be initiated only after the livestock and animal product sampling work plan is approved by MDEQ. This section details the overall sampling methodology, equipment and techniques to be employed in the livestock sampling effort, considerations for ensuring preservation of sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation, and shipping. The method of harvest will include standard butchering practices, hand collection of eggs, or milking of cows.

For each livestock animal harvested or animal product collected, the following field observations and measurements will be recorded:

- Sample ID
- Species
- Gender
- General site description
- Photographs
- GPS coordinates
- Date and time of harvest
- Collectors initials

After recording observations and measurements, the sample will be processed as described below.

3.1 Sampling Equipment and Use

The project team will assemble and pack all equipment specified below in advance of the sampling event. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

The field equipment and supplies needed for livestock or animal product sample collection may include:

- SOP for livestock and animal product sampling
- Site Health and Safety Plan
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Detailed maps of sampling site locations
- Pencils/Pens
- Sharpie waterproof markers
- Waterproof field notebook and clipboard
- Field Sampling Checklist
- Chain of custody (COC) forms
- Field data documentation forms
- Sample labels and sample tags
- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- 2-way radio and/or cell phone
- GPS receiver
- Digital camera
- Appropriate field clothing
- Duct tape
- Garbage bags
- Packing tape
- Freezer tape
- String
- Plastic sheeting
- Several sizes of plastic bags for holding individual samples
- Large plastic Ziploc bags
- Aluminum foil (extra heavy duty)
- Gloves
- Holding trays
- Automatic feather plucker
- Absorbent pads
- Masks
- Goggles
- Disposable lab coats
- Rain gear
- Coolers
- Ice (wet ice, blue ice packets, or dry ice)
- Filament-reinforced tape to seal ice chests for transport to the central processing laboratory
- Sample preservation and shipping supplies
- Tape measure
- Agent grade acetone and hexane
- Chemically clean glass I-CHEM jars (1000, 500, 250 ml capacity)
- Top loading balance

- Mops and Bleach

3.2 Sample Location and Timing

Livestock and animal product sampling will occur along the Tittabawassee River or upstream of Midland at locations where each livestock is raised or has been placed. All sample sites ultimately chosen will be located downstream of Midland. Five collection sites will be identified and the owners enlisted in the study. If no such sites are located, or owner cooperation cannot be secured, Dow representatives will discuss with the MDEQ other options to address these data. The location (*i.e.*, latitude and longitude) of each sampling location will be recorded on each field data sheet. If a Global Positioning System unit is used to provide location information, the accuracy or design confidence of the unit will be noted. Livestock or animal products will be sampled in accordance with the planned use of the meat, eggs, or milk by the owner, or after sufficient time has elapsed to establish a steady state body burden by animals placed on specific properties.

3.3 Sampling Procedure

This section details the overall sampling methodology, equipment, and techniques to be employed in the livestock or animal product sampling.

3.3.1 Cattle and Pigs

A. Cattle and pigs will be harvested according to the owner's planned use of the animal or after sufficient time has elapsed to establish a steady state body burden by animals placed on specific properties. Animals will be slaughtered and butchered in accordance with humane practices and in compliance with state agricultural regulations. If study personnel participate in the harvest, they will likewise use humane practices and comply with state agricultural regulations.

B. If owner-harvested meat animals are used; the owner will bring the animals to a local slaughterhouse for sample collection. The sampling team will record the location from which each animal was harvested. Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimen and weight, size, gender, and other information deemed useful will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time, and collector initials.

E. The animal carcass will be dressed according to standard butchering practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each carcass is dressed.

F. Specific organs (*i.e.*, liver) will be removed, weighed and then rinsed with distilled water to remove any foreign debris and/or fur that may have come into contact with the tissue during butchering. Following butchering these tissues and the edible meat described below will be placed in labeled plastic bags and transported to a clean room facility of additional processing. At this stage, approximately 1000 g of each tissue will be retained and cut into approximately 1-inch cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled.

G. After butchering, edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area, and similarly rinsed with distilled water to remove foreign debris or dirt that may have come into contact with the tissue during field dressing. At the interim processing facility, each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group/species, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close a possible. A duplicate set of muscle samples from the same areas will be collected and preserved for possible studies of cooking loss.

H. The actual weights for each muscle/meat group/species will be recorded in the appropriate field notebook and then transferred into a single chemically clean, 1000-mL I-Chem jar.

I. Beef and pork muscle and organ tissue samples in I-CHEM jars will be immediately placed on ice.

J. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.3.2 Chicken

A. Chickens will be purchased following the end of the egg collection and butchered following humane harvest and in compliance with state agricultural regulations.

B. After a harvesting is complete, the location of each harvested chicken will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Chickens will be tagged with pre-printed sample labels. One sample label will be attached to a limb of the chicken and one sample label will be attached to the bag in which the chicken carcass is placed.

D. Digital photographs will be taken of the specimen and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time and collector initials.

F. After placing the chicken carcass in the appropriate collection bag, the animal will be transported to the interim preparation facility.

G. Before dressing, chickens will be weighed to the nearest ounce.

H. Weight and sex of the chickens will be recorded in the appropriate field laboratory notebook.

I. Chickens will be dressed according to consumer practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone or hexane before the chicken is dressed. An automatic feather plucker will be used to dress the chickens.

J. Edible portions of the muscle tissue will be removed from the chicken, and rinsed with distilled water to remove any foreign debris that might have contacted the tissue during dressing. Specifically, muscle tissue will be removed from the chest and leg regions of the chicken. Approximately 350g of white meat will be removed from the breast, and approximately 150 g of dark meat will be removed from the legs. Two or more chickens from the same location may be composited together to achieve the required tissue weight and provide for duplicate samples. A duplicate set of muscle samples from the same areas will be collected and preserved for possible studies of cooking loss.

K. All muscle samples will be cut into approximately 1-inch cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is recorded and then transferred into a single chemically clean, 1000-mL I-Chem jar.

L. Chicken muscle samples in I-CHEM jars will be immediately placed on ice.

M. The remainder of each carcass will be placed in a plastic bag and stored frozen until the end of the study.

3.3.3 Chicken Eggs

A. Chicken eggs will be collected as described above (once or twice a week for a month four times a year).

B. After a harvesting period, the location from which the eggs were collected will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Eggs will be placed in a standard egg carton and the carton tagged with pre-printed labels. One sample label will be placed on the outside of the carton, the carton will be placed in a plastic bag, and another sample label will be attached to the bag in which the carton is placed.

D. Digital photographs will be taken of the specimens and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, date, time, and collector initials.

F. After placing the egg samples in the carton and the carton into appropriate collection bag, the samples will be placed on ice and transported to the interim preparation facility.

G. Before processing, egg specimens will be weighed to the nearest ounce.

H. Weight of the eggs will be recorded in the appropriate field laboratory notebook.

I. Eggs will be rinsed in distilled water to remove foreign debris. All surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone or hexane before and after processing.

J. The eggs will be cracked and the contents placed into pre-labeled, chemically clean I-CHEM jars (500 or 1000 ml capacity). The collective weight will be recorded in the field notebook. A duplicate set of egg samples from the same property will be collected and preserved for possible studies of cooking loss.

K. Composited egg samples in I-CHEM jars will be immediately placed on ice.

L. The remainder of any composited egg sample will be placed into a container and stored frozen until the end of the study.

3.3.4 Cow's Milk

A. Cow's milk will be collected as described as described above (once or twice a week for a month four times a year).

B. After a harvesting period, the location from which the milk was collected will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Milk will be placed in 1000 mL chemically clean containers (up to one gallon per cow) and each container will be tagged with pre-printed labels. One sample label will be

placed on the outside of the container, the container will be placed into a plastic bag, and another sample label will be attached to the bag in which the container is placed.

D. Digital photographs will be taken of the specimens and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, date, time, and collector initials.

F. After placing the milk samples into the container and the container into appropriate collection bag, the milk samples will be placed on ice and transported to the interim preparation facility.

G. Before processing, milk samples will be weighed to the nearest ounce.

H. Weight of the milk samples from each individual cow will be recorded in the appropriate field laboratory notebook.

I. Milk samples from multiple cows on a single property may be composited for analysis if desired. All surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone or hexane before and after processing.

J. The milk collected from a single property will be composited (if desired) and the contents placed into pre-labeled, chemically clean I-CHEM jars (1000 ml capacity). The collective weight will be recorded in the field notebook. A duplicate milk sample from the same property will be collected and preserved for possible studies of cooking loss.

K. Composited milk samples in I-CHEM jars will be immediately placed on ice.

L. The remainder of any composite milk sample will be placed into a container and stored frozen until the end of the study

3.4 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is preserved by prevention of loss of contaminants already present in the tissues and prevention of extraneous tissue contamination.

All potential sources of contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. Ice chests and preparation surfaces will be scrubbed clean with detergent and rinsed with distilled water or reagent grade solvent after each use to prevent contamination. To avoid contamination from melting ice, samples will be placed in waterproof plastic bags. Sampling equipment that has obviously been contaminated will be cleaned or not be used. All utensils or equipment

that will be used directly in handling livestock, eggs, or milk will be cleaned prior to each sampling trip, rinsed in acetone and pesticide-grade hexane, and stored in aluminum foil until used. Between sampling, the field collection team will clean the preparation surfaces by rinsing them with acetone and hexane and mopping with bleach at the end of the sampling period or as necessary.

Ideally, all sample processing of collected livestock or animal products will be performed at a sample processing facility under clean room conditions to reduce the possibility of sample contamination. If sample preparation must be performed elsewhere (a commercial slaughter house), a clean area will be set up away from sources of contamination to help reduce the potential for inadvertent surface and airborne contamination of the samples. Use of a mobile laboratory or use of a portable resection table and enclosed hood would provide the best environment for sample processing in the field, and may be considered. If sample processing is conducted elsewhere, a notation will be made in the field records and on the sample processing record.

3.5 Field Recordkeeping

Thorough documentation of all field sample collection and processing activities is necessary for proper interpretation of field survey results. The data collection phase includes the completion of a various sample-tracking forms, which includes information regarding the sample collection procedures. The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel will be properly trained in these areas and perform these tasks in secure facilities.

Field personnel will document all sampling activities in accordance with the Work Plan. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing laboratory. These are 1) Field record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection and (b) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

3.5.1 Field Record Form

For each individual livestock animal or animal product that is collected, the following observations and measurements will be recorded at a minimum:

- Species
- Date and time collected
- Temperature and weather conditions
- Site location and GPS coordinates
- Sex, approximate weight, and size as needed
- Type of all tissues collected
  - Rumproast, tenderloin, and backstrap meat for beef and pork
  - Beef liver
  - Breast and leg meat for chicken
  - Chicken eggs
  - Cow's milk
- Weight/volume/number of all tissue collected
- Collectors name(s) and signatures
- Affiliation (including telephone number and address)

3.5.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format. The QA/QC samples will be labeled accordingly.

Each sample label will have a unique sample identification number consisting of: a two-letter prefix to distinguish the project ID, a 2-digit number to distinguish location, a two-letter abbreviation for the livestock species or animal product, and a 2-digit number to designate animal number. In addition, tissue samples will be labeled 'L' or 'M' for liver or muscle accordingly. Field and laboratory blanks will be labeled with the project ID, date, and type of blank that are being collected. Example ID labeling schemes are illustrated below.

Example Livestock/Animal Product Sample ID Labels

TR01DR01
TR = Tittabawassee River Project
01 = Location Reference
BF = Beef; **PG** = Pig; **CK** = Chicken; **EG** = Chicken Egg; **MK** = Cow's Milk
01 = Animal number

TR01DR01L1
TR = Tittabawassee River Project
01 = Location Reference
BF = Beef; **PG** = Pig; **CK** = Chicken; **EG** = Chicken Egg; **MK** = Cow's Milk
01 = Animal number
L, M = Liver or Muscle tissue
1,2,3… = Replicate tissue sample number

TRMMDDBAB01
TR = Tittabawassee River Project
MMDD = Date (Month and Day only)
BAB = Blank sample type

- BAB = Butchering Atmospheric Blank
- BSR = Butchering Start Rinsate
- BER = Butchering End Rinsate
- HAB= Homogenate Atmospheric Blank
- HSR = Homogenate Start Rinsate
- HER = Homogenate End Rinsate

01 = Replicate number

A completed sample identification label will be taped to each container and the individual specimen will be placed in a waterproof plastic bag.

3.5.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual livestock or animal product specimen. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling date/time
- Processing and analysis requested
- Preservation method (wet/dry ice)

After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual sample. Information on the COC label will also be recorded on the COC form.

3.5.4 Chain-of-Custody Form

Livestock or animal product samples collected for analysis will be tracked in the field and in transit to the processing laboratory and then to the analytical laboratory. Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g.*, ice chest) used. All pertinent information will be

entered into the chain-of-custody form in the field including in-transit and laboratory delivery relinquishment/receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for tissue samples; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight, or in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

3.5.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, weather conditions, equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the livestock or animal product sample data. This will also include method of collection/harvest, start time, ending time, sampling duration, sampling location, and sampling conditions.

3.6 Sample Handling

3.6.1 Initial Field Preparation and Sorting

Tissue from the selected livestock species or animal products will be rinsed in nanopure water to remove any foreign material or blood from the external surface where necessary. Equipment used in processing samples for organics analysis will be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Tissue preparation will be done on glass or PTFE cutting boards that are cleaned properly between sample preparations or on cutting boards covered with heavy-duty aluminum foil that is changed after each sample preparation. Tissue will be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with

knives with titanium blades and PTFE handles. Samples will be stored in sealed glass containers as noted.

Prior to preparing each sample, utensils and containers will be washed with detergent solution, rinsed with tap water, soaked in reagent-grade hexane or acetone, and rinsed with nanopure water. Work surfaces will be cleaned with reagent-grade hexane or acetone, washed with distilled water, and allowed to dry completely. Knives, measurement boards, etc., will be cleaned with reagent-grade hexane or acetone followed by a rinse with contaminant-free distilled water between each livestock or animal product sample.

All livestock or animal product samples will be stored in pre-cleaned containers that are of sufficient size for sample content as described above. All sample jars used are ordered as pre-cleaned and QA/QC grade. If jars are not pre-cleaned and QA/QC grade, then they will be reagent grade acetone and hexane rinsed before use. After the jars have been dried they will be sealed and stored until needed.

3.6.2 Length or Weight Measurements

Each individual livestock species will be measured to determine total body length and weight from each sampling location, and the information recorded on the appropriate forms. Animal product samples will be weighed or measured individually before compositing and the number and amount of material that furnished the composite sample per location will be recorded

3.6.3 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PCDD/PCDF congeners as if it were an actual sample. Field blanks will be submitted at a rate of five percent of the total number of samples to conform to US EPA's recommendations. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for livestock or animal product samples will consist of muscle homogenates from livestock species or samples of the eggs and milk collected spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8- TCDF. MS/MSD analyses of homogenates from other livestock tissue samples (*i.e.*, liver) will be performed if these tissues are included in the analyses.

3.7 Sample Packaging

After sample processing, each sample will be individually stored in chemically clean glass containers. The sample identification label will be taped to the outside of each container, each container will be placed into a waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual samples for the same species from the sample location will be kept

together (if possible) in one large waterproof plastic bag in the same shipping container (ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

3.8 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed. Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours. If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer unit will be used for temporary storage of livestock or animal product samples and remaining tissue at the interim preparation facility location. Long-term storage of additional tissue or samples (until study termination) will take place at a storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University or an equivalent facility where they will be stored at –20°C until homogenization. All samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures previously specified.

3.9 Sample Shipping to Processing Facility

The various tissue samples will be hand-delivered or shipped to the processing location as soon as possible after collection and initial field processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples will be transported within 48 hours for processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a

polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

4.0 FINAL SAMPLE PREPARATION AND SHIPPING

4.1 Sample Receipt and Chain-of-Custody

Livestock and animal product samples will be shipped or hand-carried from the field and delivered to a processing location for further sample processing. Sample processing and distribution for analysis ideally will be performed by one processing location. Transportation of samples from the field will be coordinated between the sampling team supervisor and the supervisor responsible for sample processing and distribution. An accurate written custody record will be maintained so that possession and treatment of each sample can be traced from the time of collection through analysis and final disposition.

Livestock and animal product samples will be brought (or shipped) to the sample processing location in sealed containers accompanied by a copy of the sample request form, a chain-of-custody form, and the field records. Each time custody of a sample or set of samples is transferred; the Personnel Custody Record of the COC form will be completed and signed by both parties. Corrections to the COC form will be made in indelible ink by drawing a single line through the original entry, entering the correct information and the reason for the change, and initialing and dating the correction. The original entry should never be obscured.

When custody is transferred from the field to the sample processing location, the following procedure will be used:

• Shipping time will be noted (has the shipping time exceeded the appropriate time for preservation method used?).
• Check that each shipping container has arrived undamaged and that the seals are intact.
• Open each shipping container and remove the copy of the sample request form, the COC form, and the field records.
• Note the general condition of the shipping container (samples iced properly with no leaks, etc.) and the accompanying documentation (dry, legible, etc.).
• Locate individual samples listed on the COC form and note the condition of their packaging. Individual specimens should be properly wrapped and labeled. Note any problems (container broken, illegible labels, etc.) on the COC form.
• If individual samples are packaged together, check the contents of each composite sample container against the field record for that sample to ensure that the individual specimens are properly packed and labeled. Note any discrepancies or missing information on the COC form.
• Initial the COC form and record the date and time of sample receipt.
• Enter the following information for each composite sample into a permanent laboratory record book and, if applicable, a computerized database:

1 Sample identification number (specify conventions for specimen number)
2 Receipt date (YYYYMMDD)

3 Sampling date (YYYYMMDD)
4 Sampling site (name and/or identification number)
5 Livestock species or animal product (scientific name or code number)
6 Weight of sample

• If samples have been shipped on wet or blue ice, distribute them immediately to the technician responsible for sample preparation. If samples have been shipped on dry ice, they may be distributed immediately to the technician for processing or stored in a freezer at -20^{o} C for later processing. Once processed, samples should be stored according to the procedures described below.

4.2 Sample Processing

A. Livestock and animal product tissue samples received by the processing location will be stored at –20°C until they are ready for homogenization. Replicate samples or samples not immediately needed for sampling will be stored under the same conditions.

B. To ensure even distribution of contaminants throughout tissue samples and to facilitate extraction and digestion of samples, the sample will be ground and homogenized prior to being sent to the analytical laboratory for analysis. Previously cubed livestock samples will be ground and homogenized in stainless steel blenders. Grinding and homogenization of tissue may be easier when it is partially frozen. Chilling the grinder/blender briefly with a few chips of dry ice may also help keep the tissue from sticking to it. The livestock sample will be ground until it appears to be homogeneous. The ground sample should then be divided into quarters, opposite quarters mixed together by hand, and the two halves mixed together. The grinding, quartering, and hand-mixing steps should be repeated at least two more times. If chunks of tissue are present at this point, the grinding and homogenization will be repeated. Liquid animal product samples (eggs and milk) will also be homogenized prior being divided into aliquots

The preparation of each individual homogenate will be noted on the sample processing record. At this time, individual homogenates may be frozen separately. The sample processing location will prepare aliquots of the individual homogenates for analysis, distribute the aliquots to the appropriate laboratory, and archive the remainder of each homogenate along with the remaining tissue. Before, during, and after sample preparation, blenders will be washed with Liquinox soap, rinsed three times with distilled water, and reagent grade acetone and hexane rinsed. Other equipment and surfaces that may potentially contact the sample will be likewise cleaned regularly. Verification of the efficacy of cleaning procedures may be documented through the analysis of processing blanks or rinsates.

C. Homogenates will be aliquoted into four to six separate chemically clean I-CHEM jars according to the amount of the sample. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived. Remaining homogenates will be labeled and stored frozen. Sample IDs will be labeled for each replicate homogenate sample as described above.

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

The actual sample size required will depend on the analytical method used and the laboratory performing the analysis. Therefore, the exact sample size required for each type of analysis will be determined in advance with the analytical laboratory selected. The frozen aliquot(s) will be transferred on dry ice to the analytical laboratory accompanied by a sample transfer record. The sample transfer record will include a section that serves as the analytical laboratory COC record. The COC record will be signed each time the samples change hands for preparation and analysis.

Care will be taken during sample processing to avoid contaminating samples. This may be particularly problematic for PCDD/Fs, given the low levels that are of potential concern. Potential sources of contamination include dust, instruments, utensils, work surfaces, and containers that may contact the samples. All sample processing will be done in an appropriate laboratory facility under clean room conditions. Clean rooms or work areas will be free of organic contaminants. Periodic wipe tests may be conducted in clean areas to verify the absence of significant levels of organic contaminants. All instruments, work surfaces, and containers used to process samples will be of materials that can be cleaned easily.

4.3 Sample Shipping to Analytical Laboratory

Tissue homogenates, field blanks, and MS/MSD samples will be packaged and shipped for laboratory analysis according to US EPA/REAC guidelines (US EPA, 1994) as noted above.

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples will be transported to the analytical laboratory as soon as feasible after processing. To prevent leakage during shipping, sample containers will be no more than

90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the analytical laboratory unless prior plans for such a delivery have been agreed upon with the laboratory staff. The time the samples were collected and time of their arrival at the analytical laboratory will be recorded on the COC form.

4.4 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD/F detected across sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, date and time of sample collection, sample and tissue type, lipid content of tissues, and PCDD/F concentrations of tissues. The data entry will be verified to ensure the accuracy of the information. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

4.5 Data Analysis

The objective of data analysis is to identify and report the PCDD/F concentrations measured in livestock species and animal products that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, or standard error), and develop a valid PDF for use in exposure and risk assessment. These steps are outlined in

the Exposure Assessment Work Plan that is currently in development and will be submitted by December 1, 2006. Ultimately, this information will be used to calculate the potential risk of PCDD/F exposure to humans.

5.0 References

Blasland, Bouck & Lee. 1999. Sampling and Analysis Plan/Data Collection and Analysis Quality Assurance Plan. Blasland, Bouck & Lee, Inc., Syracuse, NY.

US EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - US EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

Garden Vegetable Study Plan

Study Objectives

1. To identify those locations in the Midland Study Area and the Tittabawassee Study Area where undisturbed (*i.e.,* soil that has not been replaced under past remedial work) gardens are maintained and homegrown crops are raised for consumption,
2. To identify and collect an adequate number of samples of homegrown fruits and vegetables (*i.e.*, root crops, fruiting crops, leafy and waxy crops, etc.) from residential gardens within the Midland Study Area (if they exist) and the Tittabawassee Study Area most commonly grown and consumed by residents,
3. In the absence of access to private gardens, to propose alternate means to gather such information for purposes of risk assessment,
4. To identify and prepare individual edible portions of various locally-raised garden crops for analysis in the same manner as is commonly done by consumers, and
5. To submit those garden crop samples to a qualified laboratory for analysis of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans (PCDD/Fs) relevant to the Midland Study Area and the Tittabawassee River Study Area.

The Study will preserve tissue from the garden sampling in the event that additional or confirmatory sampling is required. The analytical results from the garden sampling will serve as the concentration term in the development of the probability density function (PDF) used to determine PCDD/Fs and estimate exposure through ingestion of various garden crops. The necessary data inputs, methods and decisions used to create this specific PDF will be detailed in the Exposure Assessment Work Plan. Other aspects of PCDD/F exposure through ingestion of garden crops, such as weighting the contribution of garden crops to the diet, consumption of specific garden crops, accounting for cooking loss of PCDD/Fs, and determining the frequency and rate of consumption will also be detailed in the relevant Exposure Assessment Work Plan to be submitted by December 1, 2006.

The sampling plan and methods for acquiring qualitative and quantitative data on homegrown garden crop consumption by residents in the Study Areas will be developed primarily from the planned Activity Survey and other sources of information such as the UMDES questionnaire information, or information gathered from the MDA, local extension agents, or other local sources of information developed to fill relevant data gaps that are identified. Any suggested modifications to this plan in terms of crop species, numbers, and preparation methods based on such information or suggestions will be reviewed and, if relevant, adopted in order to improve the relevance and site-specificity of the garden vegetable sampling protocol, thereby further reducing uncertainty. Planning and documentation of the sampling procedures will be done to ensure that collection activities are time and labor-effective and that sample integrity is

preserved. It is anticipated that both collection and analysis of readily available garden crops can be completed within a single growing season following approval of this work plan by MDEQ. If garden plots must be introduced into the Study Areas in order to develop such information, it may require additional time to identify the plots, gain access, and grow the crops; and this will increase the amount of time needed to complete the study.

1.0 Introduction

There are currently no data on fruit and vegetable uptake of PCDD/Fs from local gardens although published studies of plant uptake of these and related chemicals suggest the exposure potential is small with any plant residues attributable to airborne deposition and not via translocation through the roots. The lack of site-specific data makes it difficult to draw firm conclusions about the actual human health risks posed by potential consumption of garden fruits and vegetables raised locally. Since Study Area residents, their families, and others may consume homegrown fruits and vegetables from Study Area gardens, ingestion of homegrown fruits and vegetables constitutes a potentially completed exposure pathway and requires evaluation and inclusion in the Human Health Risk Assessment (HHRA).

Since there are no site-specific data for risk assessment purposes, the Study proposes to carry out sampling to evaluate the types of vegetables most likely to be grown by homeowners in Midland and living along the river and subsequently, collect relevant and reasonable fruit and vegetable samples for analysis based on crops likely raised in local gardens for consumption (*i.e.*, carrots, potatoes, onions, tomatoes, zucchini, cucumbers, etc.). This Study will identify undisturbed gardens within the Study Area and offer to purchase part of the crop for purposes of analysis. A soil sample will be collected from the garden at the same time. The edible portion of these fruit and vegetable samples will be prepared in the manner most common to these foods, and submitted for analysis. Sufficient samples would be retained to repeat the analysis or conduct studies of cooking loss, if needed. The extent of Midland and Tittabawassee Study Area homegrown fruit and vegetable consumption, frequency and duration of ingestion, and preparation methods will be determined by a planned Activity Survey. Interviews with local residents, local extension agents, and the Michigan Department of Agriculture (MDA) and the results of the University of Michigan Dioxin Exposure Study (UMDES) will supplement this information.

It should be noted that it is possible that access to undisturbed gardens may not be granted. In such a case, Dow will confer with MDEQ on alternate approaches to gathering useful information on this route of exposure. These may include 1) planting selected garden crops on screened private properties (with the cooperation of property owners) that have representative PCDD/F residues and raising the crops on those properties until normal harvest or 2) planting select garden crops on Dow-owned properties and raise the crops on those properties until normal harvest.

2.0 SAMPLING DESIGN FOR COLLECTING GARDEN CROPS, SIZE, LOCATION, AND CONCENTRATION DATA.

Development of the final garden-sampling plan that is site-specific, reasonable, and relevant will rely upon input from the Activity Survey, the UMDES results, MDA experts, extension agents, and local residents. In addition to collecting samples from the relevant garden crops, the study protocol provides recommendations on sample preparation so that the HHRA can be based on actual amounts of PCDD/Fs in garden crops consumed by residents. The primary considerations for this sampling effort are public safety, collection of a representative and robust set of garden crop samples, chain-of-custody, and sample integrity issues.

There are six major parameters that will be specified prior to the initiation of the field collection activities:

- Site selection
- Target plant species
- Target analytes (PCDD/Fs)
- Target analyte screening values
- Sampling times
- Sample type

These parameters will be documented on a sample form prepared for each sampling location found in the Tittabawassee or Midland Study Area. The sample form will provide the sampling team with readily available information on the study objective, site location, site name/number, target tissue or product to be collected, number of individual samples to be collected, sampling and preparation method to be used, target analytes (PCDD/Fs) to be evaluated, sampling date, and number of replicates to be collected. The sampling manager will retain the original sample forms and a copy kept with the field logbook.

2.1 Site Selection

Sampling locations for garden crops in the Tittabawassee Study Area and within the Midland Study Area will be selected based on the existence of gardens used to provide vegetables and fruits for human consumption identified from the Activity Survey, the UDMES questionnaire, or through observation of, or information from, local residents and state or county experts. The final areas for consideration would include areas where soil contamination exists, and where gardens are grown in undisturbed soils. Modification of initial garden selection may occur upon interview results or recommendation of local experts as necessary.

The procedures required to identify garden sites will be straightforward. All sampling will be conducted within the Study Areas. Some garden crops will be collected from gardens upstream of Midland to provide reference information. Additional garden locations will be chosen based on responses to the Activity Survey as well as information

gathered by the UMDES and provided by MDA or local agricultural experts. A composite sample consisting of five soil samples (0" – 6"), collected from each corner and the center of the garden will be prepared for each garden. Any soil samples collected near each garden location will also be identified and the analytical results arrayed to examine the possibility of correlating contaminant concentrations between different environmental media (*i.e.*, soil and garden crops). If no sampling points exist in or near the garden location, additional soil samples will be collected from the garden or property for comparison. Potential garden locations where the resident refuses soil sampling will not be used.

The final selection of both the number, type, and location of garden samples will be based on information about the type and numbers of crops raised, specific properties where they are raised, willingness to cooperate with the study among property owners, timing of harvest for crop samples, and consumption patterns among residents. Once the various sampling sites have been selected, they will be plotted and numbered on the existing Geographic Information System (GIS) using a Global Positioning System (GPS). It is conceivable that properties where gardening is done may not be accessible or useful either because no garden exists at the moment or access is denied. In such a case, Dow may propose to carry out additional experimental work to assess this route of exposure. Dow may either locate a model garden on privately owned land along the river, or Dow property and raise crops there over the normal growing period followed by harvest and analysis.

2.2 Target Garden Crop Selection

The garden crops selected for this site-specific study are those most commonly raised and ingested in the diet: Root crops such as carrots, onions, or potatoes; fruiting crops such as tomatoes or peppers; crops with waxy outer layers such as cucumbers or zucchini; or leafy crops such as lettuce or cabbage. Crops that are in contact with soil or have characteristics that may increase absorption of PCDD/Fs into them would make potentially the best indicators of exposure conditions along the river or within the city.

The final selection of crops to be sampled will be based on those reported as being commonly raised from the Activity Survey responses as well as those actually planted in the growing season in which sampling will occur. Crops reported as being raised and consumed in the UMDES questionnaire or from other local sources that can be independently verified may also be used to modify the crops selected for sampling. It is anticipated that the primary focus of the garden sampling will be on a selection of those crop types named above although other crops may be included or substituted in the risk assessment process if they are raised and are available locally.

Individual samples will be collected from the targeted gardens identified in the Activity Survey and from which the property owners agree to participate. Dow anticipates selecting no more than ten properties in the city and ten along the river on which gardens are raised. Two more gardens may be sampled from upstream of Midland to gather reference samples. In the event that twenty private gardens cannot be located, they do not contain all the crop types, or access is denied, Dow will consider planting selected

crop species on city and river properties that they control or can lease or rent in order to mimic the conditions in which garden crops could be exposed to PCDD/Fs. In general, edible plant tissue will be collected following the normal growing period for the crop in question in sufficient amounts to allow retention of tissue for any additional analysis needed. In terms of specific crops from a single garden, composites of these crops will be created for analysis to estimate the exposure through consumption. A preliminary list of plant species, sample types, and number of samples per garden plant are shown in the following table.

Table 1. Garden Crop Sampling Plan by Species/Product

Target Species	Location	Sample type	# Composite Samples/Location	Total # of Samples
Root Crops (carrot, potato, onion)	10 (TR) 10 (M) 2 (RF)	Edible portion (washed & peeled)	1 1 1	10 10 2
Fruiting Crops (tomatoes, peppers)	10(TR) 10 (M) 2 (RF)	Edible portion (washed)	1 1 1	10 10 2
Waxy Crops (cucumber, zucchini)	10 (TR) 10 (M) 2 (RF)	Edible portion (washed & peeled)	1 1 1	10 10 2
Leafy Crops (lettuce, cabbage)	10 (TR) 10 (M) 2 (RF)	Edible portion (washed)	1 1 1	10 10 2

Other crop types and the number or type of samples may be added or changed based on the site-specific Activity Survey, the UMDES information or input from local residents or MDA experts.

2.3 Target Analyte Selection

The primary focus of this sampling effort is to determine the concentrations, patterns, and variability of polychlorinated dioxins and furans (PCDD/Fs) in the edible portions of various garden crops collected from the City of Midland and along the Tittabawassee River.

2.4 Target Analyte Detection Limits

The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of the target analytes in select tissue samples from garden crops collected from selected locations in Midland, along the Tittabawassee River, or reference locations. In the case of congener-specific PCDD/Fs analyses, the detection limit selected is generally in the range of 0.1 part per trillion (ppt) in view of the amount of tissue available for analysis (results to be reported on a wet weight basis). Non-detects will be handled as Limit of Detection (LOD) = 0. For crops that consistently demonstrate non-detects in a manner consistent with the upstream control vegetables, a decision will

be made whether or not these non-detects indicate no difference between upstream, downstream, or Midland-raised garden vegetables. This decision will be made in the Exposure Assessment Work Plan.

2.5 Sampling Times

Sampling will be conducted at the end of the normal growing season for the crops in question or when the first crop is ripe for continuously growing vegetables like tomatoes. Therefore, this sampling activity will coincide with the harvesting of crops from existent privately owned gardens by residents participating in this sampling activity within the City of Midland or along the Tittabawassee River during the latter part of 2006. If the work plan is not approved or no privately owned gardens can be identified or accessed, collection of garden crops will need to be delayed until the latter half of 2007. The sampling locations will be re-visited during the growing season to check on crop progress and health, and crop samples will be collected until the targeted sample amount for each crop species is attained. Possible exceptions to the recommended sampling periods for different crops will be determined by information gathered by the Activity Survey, the UMDES questionnaire information or other sources of site-specific information, or input from MDA and local residents that suggest alternative sampling periods need to be used. Therefore, the entire sampling effort will be dependent on the presence or abundance of gardens in the areas of interest, owner cooperation and accessibility of the garden, the existence of the target crop(s) within the city and along the river, access during the appropriate harvesting periods, and that the crops have been grown in soil containing the PCDD/Fs. The actual sampling for each crop species and the rationale for the sampling selection will be documented fully and the final report will include a description of sampling results.

2.6 Sample Type and Preparation

Individual or composite samples of edible portion of the selected crops will be obtained and analyzed based on crop selected and the manner of consumer preparation. The sampling objectives and approach are dependent on the targeted crop species.

For root crops such as carrots, potatoes, onions, radishes and the like, the objective will be to harvest a representative sample of a root crop that is consumed by residents that have gardens in the City of Midland or along the Tittabawassee River. A single root crop will be selected for sampling based on its prevalence in local gardens as determined by the Activity Survey and other sources of information. The Study will harvest the specific root crop selected at the same stage of growth (when ripe) at identified garden locations. Any variation on the collection of the root crop will be evaluated once the garden samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For fruiting crops like tomatoes and peppers, the objective is likewise to collect a representative sample of a fruiting crop that is consumed by residents that have gardens in the City of Midland or along the Tittabawassee River. A single fruiting crop will be selected for sampling based on its prevalence in local gardens as determined by the

Activity Survey and other sources of information. Again, the potential influences of variables such as weather or collection time will be evaluated once the garden samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For waxy crops such as cucumbers, zucchini or squash, the objective will be to sample a waxy crop that is consumed by residents that have gardens in the City of Midland or along the Tittabawassee River. A single waxy crop will be selected for sampling based on its prevalence in local gardens as determined by the Activity Survey and other sources of information. The potential influences of variables such as weather or collection time will be evaluated once the garden samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

For leafy crops such as lettuce, cabbage, kale and so forth, the objective will be to sample a leafy crop that is consumed by residents that have gardens in the City of Midland or along the Tittabawassee River. A single leafy crop will be selected for sampling based on its prevalence in local gardens as determined by the Activity Survey and other sources of information. The potential influences of variables such as weather or collection time will be evaluated once the garden samples are analyzed and, if significant, the differences will be factored into the development of weighting factors and the exposure PDFs.

A composite soil sample will also be collected from each garden participating in the sampling effort to determine how the soil PCDD/F concentrations relate to PCDD/F content of the selected crops. A 0" to 6" core sample will be collected from each corner of the garden and from the center. The five cores will be mixed and a composite sample produced that will be analyzed for PCDD/Fs. Other soil samples that may have been collected in proximity to the garden will be identified and the results included in the analysis

The preparation of the vegetables for consumption from each garden crop collected will be done to reflect the general practice among consumers and will reflect as well the preparatory steps prior to cooking or consumption. In the case of root and waxy crops, the crop will be cleaned, rinsed in water, and peeled with the peeled vegetable used for assessing exposure to members of the general population since consumers typically peel such vegetables. Samples of fruiting and leafy crops will be cleaned, rinsed in water, and left unpeeled. Consumption and use of garden crops as well as preparation methods for various garden crops and other factors that might influence residues will be verified in the site-specific Activity Survey. A sufficient amount of tissue from each garden crop harvested will be retained for possible additional analysis if cooking loss needs to be ascertained or other analysis is required for purposes of ascertaining or refining exposure estimates.

Garden crops identified as part of the sample will be harvested in accordance with the normal ripening cycle. These crops will be sorted by species, size, and sample location in accordance with sample handling procedures detailed below. After samples have been collected and initial documentation has been completed, samples will be processed at a interim processing facility as is normally done to avoid contamination. In this facility,

crops will be prepared according to standard practices. The following sections briefly discuss the processing procedures.

It is the intention of this study to sample existing gardens maintained by area residents, if possible. During the study period, the study will locate these properties and owners and offer to buy a portion of those garden crops that are targeted for sampling and analysis. Alternatively, the study will pay local gardeners to raise the desired crops on their property. In either case, study representatives will be on hand at the time of harvest to collect the relevant samples (approximately four pounds of each crop per garden). For each crop type, the approximate weight of the crop and time of planting and harvest will be recorded. The individual crop samples will be placed in re-sealable plastic bags and be transported to an interim facility for further processing. At this facility, the exterior of all crops harvested for purposes of analysis will be rinsed with distilled water to remove foreign debris, soil, etc. Root and waxy crops will be peeled. Depending on the amount of each crop collected and tissue available after processing, up to 1000 g will be cut into small cubes (approximately 1 cubic inch), weighed, and transferred into a chemically clean, 1 L I-CHEM jar. A duplicate set of samples will be collected and retained for possible evaluation of cooking loss or other issues. All of the crop samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU) or an equivalent facility. At this facility, samples will be stored at -20^{o}C where a subset will be homogenized. Once homogenized, the samples will be separated into six aliquots and transferred into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived. Splits will be made available to MDEQ upon request.

3.0 SAMPLE COLLECTION AND INITIAL PREPARATION

The primary purpose of this sampling is to collect sufficient tissue from the edible portions of select garden crops prepared in a manner relevant to human consumption that can be used to determine the concentration of congener-specific PCDD/Fs. Sufficient crop samples will be retained to analyze separately if needed or to conduct studies on the effects of cooking on the loss of PCDD/Fs. Garden crops will be collected within various areas of the City of Midland and along the Tittabawassee River and will be harvested according to normal patterns of use, so that the sampling effort will represent typical consumption activities and exposure patterns. MDEQ will be notified of sampling dates and locations prior to actual collection of samples as requested.

Sample collection activities will be initiated only after the garden vegetable sampling work plan is approved by MDEQ. This section details the overall sampling methodology, equipment and techniques to be employed in the garden crop sampling effort, considerations for ensuring preservation of sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation, and shipping. The method of harvest will be by hand collection of garden crops at time of ripening.

For each select crop type harvested, the following field observations and measurements will be recorded:

- Sample ID
- Crop
- Garden location
- General site description
- Photographs
- GPS coordinates
- Date and time of harvest
- Collectors initials

After recording observations and measurements, the sample will be processed as described below.

3.1 Sampling Equipment and Use

The project team will assemble and pack all equipment specified below in advance of the sampling event. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

The field equipment and supplies needed for garden crop sample collection may include:

- SOP for garden sampling

- Site Health and Safety Plan
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Detailed maps of garden locations
- Pencils/Pens
- Sharpie waterproof markers
- Waterproof field notebook and clipboard
- Field Sampling Checklist
- Chain of custody (COC) forms
- Field data documentation forms
- Sample labels and sample tags
- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- 2-way radio and/or cell phone
- GPS receiver
- Digital camera
- Appropriate field clothing
- Duct tape
- Garbage bags
- Packing tape
- Freezer tape
- String
- Plastic sheeting
- Several sizes of plastic bags for holding individual samples
- Large plastic Ziploc bags
- Aluminum foil (extra heavy duty)
- Gloves
- Holding trays
- Knives
- Vegetable peeler
- Soil Corer
- Absorbent pads
- Masks
- Goggles
- Disposable lab coats
- Rain gear
- Coolers
- Ice (wet ice, blue ice packets, or dry ice)
- Filament-reinforced tape to seal ice chests for transport to the central processing laboratory
- Sample preservation and shipping supplies
- Tape measure
- Reagent grade acetone and hexane
- Chemically clean glass I-CHEM jars (1000, 500, 250 ml capacity)

- Top loading balance
- Mops and Bleach

3.2 Sample Location and Timing

Garden sampling will occur in the City of Midland, along the Tittabawassee River, or upstream of Midland at locations in which gardens are located or have been placed. Ten garden sites will be identified in the city and along the river and the owners enlisted in the study. Two reference gardens will be located upstream of Midland for comparison. If no such existent (undisturbed) gardens are located, or owner cooperation cannot be secured, consideration will be given to raising the selected crops on Dow-owned, leased, or rented properties to enable this exposure pathway to be properly assessed. The location (*i.e*., latitude and longitude) of each garden will be recorded on each field data sheet. If a Global Positioning System unit is used to provide location information, the accuracy or design confidence of the unit will be noted. Garden crops will be sampled in accordance with the planned normal use of such crops by the owner.

3.3 Sampling Procedure

This section details the overall sampling methodology, equipment, and techniques to be employed in the garden sampling.

3.3.1 Root Crops

A. In conjunction with MDEQ, a specific root crop will be selected to be representative for all other root crops. The root crop will be harvested after sufficient time has elapsed to allow for normal ripening in each garden. Root crops will be dug up by hand, loose dirt removed and placed separately in chemically clean glass jars, and a minimum of five pounds of vegetables will be placed in pre-labeled, re-sealable plastic bags for transport to a processing location.

B. The sampling team will record the location from which the root crop was harvested. Other environmental parameters, such as condition of the plants and garden, time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimens; weight and other information will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: crop type, location, date, time, and collector initials.

E. The root crop will be prepared according to typical culinary practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each sample is prepared.

F. The root crop sample will be placed in labeled plastic bags and transported on ice to a clean room facility for additional processing. The root crop sample will be removed from the bag, weighed and then rinsed with distilled water to remove any foreign debris or soil that may still be clinging to the surfaces. Normal washing techniques such as are used in the home will be employed to clean the root crop. Following cleaning, the root crop will be peeled using a standard kitchen peeler. The individual plants collected will be used to develop a composite sample for this crop type. At this stage, approximately 1000 g of tissue will be sliced into approximately 1-inch cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled. The last cube to be added will be trimmed until the target weight is achieved as close as possible. A duplicate set of root crop samples from the same garden will be collected and preserved for possible studies of cooking loss.

G. Root crop samples in I-CHEM jars will be immediately placed on ice.

H. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.3.2 Waxy Crops

A. In conjunction with MDEQ, a specific waxy crop will be selected to be representative for all other waxy crops. The waxy crop will be harvested after sufficient time has elapsed to allow for normal ripening in each garden. Waxy crops will be collected by hand, loose dirt removed, and a minimum of five pounds of the vegetable will be placed in pre-labeled, re-sealable plastic bags for transport to a processing location.

B. The sampling team will record the location from which the waxy crop was harvested. Other environmental parameters, such as condition of the plants and garden, time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimens; weight and other information will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: crop type, location, date, time, and collector initials.

E. The waxy crop will be prepared according to typical culinary practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each sample is prepared.

F. The waxy crop sample will be placed in labeled plastic bags and transported on ice to a clean room facility for additional processing. The waxy crop sample will be removed from the bag, weighed, and then rinsed with distilled water to remove any foreign debris or soil that may still be clinging to the surfaces. Normal washing techniques such as are

used in the home will be employed to clean the crop. Following cleaning, the crop will be peeled using a standard kitchen vegetable peeler. The individual plants collected will be used to develop a composite sample for this crop type. At this stage, approximately 1000 g of crop tissue will be sliced into approximately 1-inch cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled. The last cube to be added will be trimmed until the target weight is achieved as close as possible. A duplicate set of waxy crop samples from the same garden will be collected and preserved for possible studies of cooking loss.

G. Waxy crop samples in I-CHEM jars will be immediately placed on ice.

H. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.3.3 Fruiting Crops

A. In conjunction with MDEQ, a specific fruiting crop will be selected to be representative for all other fruiting crops. The fruiting crop will be harvested after sufficient time has elapsed to allow for normal ripening in each garden. Fruiting crops will be collected by hand, loose dirt removed, and a minimum of five pounds will be placed in pre-labeled, re-sealable plastic bags for transport to a processing location.

B. The sampling team will record the location from which the fruiting crop was harvested. Other environmental parameters, such as condition of the plants and garden, time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimens; weight and other information will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: crop type, location, date, time, and collector initials.

E. The fruiting crop will be prepared according to typical culinary practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each sample is prepared.

F. The fruiting crop sample will be placed in labeled plastic bags and transported on ice to a clean room facility for additional processing. The fruiting crop sample will be removed from the bag, weighed and then rinsed with distilled water to remove any foreign debris or soil that may be clinging to the surfaces. Normal washing techniques such as are used in the home will be employed to clean the fruiting crop. The individual plants collected will be used to develop a composite sample for this crop type. At this stage, approximately 1000 g of the crop tissue will be sliced into approximately 1-inch cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled. The last cube to be added will be trimmed until the target weight is achieved as

close as possible. A duplicate set of fruiting crop samples from the same garden will be collected and preserved for possible studies of cooking loss.

G. Fruiting crop samples in I-CHEM jars will be immediately placed on ice.

H. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.3.4 Leafy Crops

A. In conjunction with MDEQ, a specific leafy crop will be selected to be representative for all other leafy crops. The leafy crop will be harvested after sufficient time has elapsed to allow for normal ripening in each garden. Leafy crops will be collected by hand, loose dirt removed, and a minimum of five pounds will be placed in pre-labeled, re-sealable plastic bags for transport to a processing location.

B. The sampling team will record the location from which the leafy crop was harvested. Other environmental parameters, such as condition of the plants and garden, time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the specimens; weight and other information will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: crop type, location, date, time, and collector initials.

E. The leafy crop will be prepared according to typical culinary practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each sample is prepared.

F. The leafy crop sample will be placed in labeled plastic bags and transported on ice to a clean room facility for additional processing. The leafy crop sample will be removed from the bag, weighed and then rinsed with distilled water to remove any foreign debris or soil that may be clinging to the surfaces. Normal washing techniques such as are used in the home will be employed to clean the leafy crop. The individual plants collected will be used to develop a composite sample for this crop type. At this stage, approximately 1000 g of the crop tissue will be sliced into approximately 1-inch segments and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled. The last portion to be added will be trimmed until the target weight is achieved as close as possible. A duplicate set of leafy crop samples from the same garden will be collected and preserved for possible studies of cooking loss.

G. Leafy crop samples in I-CHEM jars will be immediately placed on ice.

H. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.3.5 Garden Soil

A. At the same time the garden crop samples are collected, a composite sample of the garden soil in which they were raised will also be collected. Five cores (0" to 6") will be collected from each corner and the center of each garden. Soil samples will be collected using a standard soil-coring tool. The cores from each garden will be placed in a pre-labeled, chemically clean glass jar. The jars will be placed in pre-labeled, re-sealable plastic bags for transport to a processing location.

B. The sampling team will record the location from which the soil was collected. Environmental and other parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Digital photographs will be taken of the garden and soil collection; other information deemed useful will be recorded.

D. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time, and collector initials.

E. All surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane and water before each sample is prepared.

F. The soil sample will be thoroughly mixed by hand at the processing facility. At this stage, approximately 1000 g of the composite soil sample will be transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled.

G. The soil samples placed into the I-CHEM jars will be immediately placed on ice.

H. Mops and bleach solution will be used to clean the preparation area following daily activities.

3.4 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is preserved by prevention of loss of contaminants already present in the tissues and prevention of extraneous tissue contamination.

All potential sources of contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. Ice chests and preparation surfaces will be scrubbed clean with detergent and rinsed with distilled water or reagent grade solvent after each use to prevent contamination. To avoid contamination from melting ice,

samples will be placed in waterproof plastic bags. Sampling equipment that has obviously been contaminated will be cleaned or not be used. All utensils or equipment that will be used directly in handling garden crops or garden soil will be cleaned prior to each sampling trip, rinsed in acetone and reagent-grade hexane, and stored in aluminum foil until used. Between sampling, the field collection team will clean the preparation surfaces by rinsing them with acetone and hexane and mopping with bleach at the end of the sampling period or as necessary.

Ideally, all processing of collected garden crop samples will be performed at a sample processing facility under clean room conditions to reduce the possibility of sample contamination. If sample preparation must be performed in the field, a clean area will be set up away from sources of contamination to help reduce the potential for inadvertent surface and airborne contamination of the samples. Use of a mobile laboratory would provide the best environment for sample processing in the field, and may be considered. If sample processing is conducted elsewhere, a notation will be made in the field records and on the sample processing record.

3.5 Field Recordkeeping

Thorough documentation of all field sample collection and processing activities is necessary for proper interpretation of field survey results. The data collection phase includes the completion of various sample-tracking forms, which includes information regarding the sample collection procedures. The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel will be properly trained in these areas and perform these tasks in secure facilities.

Field personnel will document all sampling activities in accordance with the Work Plan. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be developed and used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing laboratory. These are 1) Field record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) date and time of collection and (b) collectors initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

3.5.1 Field Record Form

For each individual crop type that is collected from an individual garden, the following observations and measurements will be recorded at a minimum:

- Crop type
- Date and time collected
- Temperature and weather conditions
- Site location and GPS coordinates
- Approximate weight
- Type of all tissues collected
- Number of plants collected
- Collectors name(s) and signatures
- Affiliation (including telephone number and address)

3.5.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format. The QA/QC samples will be labeled accordingly.

Each garden sample label will have a unique sample identification number consisting of: a two-letter prefix to distinguish the project ID, a 2-digit number to distinguish location, a two-letter abbreviation for the crop, and a 2-digit number to designate garden number. Any replicate samples will carry an additional digit. Field and laboratory blanks will be labeled with the project ID, date, and type of blank that are being collected. Example ID labeling schemes are illustrated below.

Example Garden Sample ID Labels

TR01DR01
TR = Tittabawassee River Project
00 = Location Reference (01 = River; 02 = Midland; 03 = Reference)
CA = Carrot; **PO** = Potato; **ON** = Onion; **RD** = Radish; **TO** = Tomato; **PE** = Pepper; **CU** = Cucumber; **ZU** = Zucchini; **LE** = Lettuce; **CA** = Cabbage
00 = Garden number (01- 12)

TR01DR01-1
TR = Tittabawassee River Project
00 = Location Reference (01 = River; 02 = Midland; 03 = Reference)
CA = Carrot; **PO** = Potato; **ON** = Onion; **RD** = Radish; **TO** = Tomato; **PE** = Pepper; **CU** = Cucumber; **ZU** = Zucchini; **LE** = Lettuce; **CA** = Cabbage
01 = Garden Number
1,2,3… = Replicate tissue sample number

TRMMDDPAB-1
TR = Tittabawassee River Project
MMDD = Date (Month and Day only)
BAB = Blank sample type

- PAB = Processing Atmospheric Blank
- PSR = Processing Start Rinsate
- PER = Processing End Rinsate
- HAB= Homogenate Atmospheric Blank
- HSR = Homogenate Start Rinsate
- HER = Homogenate End Rinsate

1 = Replicate number

A completed sample identification label will be taped to each container and the individual specimen will be placed in a waterproof plastic bag.

3.5.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual garden crop sample specimen. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling date/time
- Processing and analysis requested
- Preservation method (wet/dry ice)

After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual sample. Information on the COC label will also be recorded on the COC form.

3.5.4 Chain-of-Custody Form

Garden crop samples collected for analysis will be tracked in the field and in transit to the processing laboratory and then to the analytical laboratory. Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g.*, ice chest) used. All pertinent information will be entered into the chain-of-custody form in the field including in-transit and laboratory delivery

relinquishment/receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for tissue samples; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight or in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

3.5.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, weather conditions, equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the garden crop sample data. This will also include method of collection/harvest, start time, ending time, sampling duration, sampling location, and sampling conditions.

3.6 Sample Handling

3.6.1 Initial Field Preparation and Sorting

Tissue from the selected garden crops will be rinsed in distilled water to remove any foreign material from the external surface. Equipment used in processing samples for organics analysis will be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Sample preparation will be done on glass or PTFE cutting boards that are cleaned properly between sample preparations or on cutting boards covered with heavy-duty aluminum foil that is changed after each sample preparation. Tissue will be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles. Samples will be stored in sealed glass containers as noted.

Prior to preparing each sample, utensils and containers will be washed with detergent solution, rinsed with tap water, soaked in reagent-grade hexane or acetone, and rinsed with distilled water. Work surfaces will be cleaned with reagent-grade hexane or acetone, washed with distilled water, and allowed to dry completely. Knives, measurement boards, etc., will be cleaned with reagent-grade hexane or acetone followed by a rinse with distilled water between each garden crop sample.

All garden crop samples will be stored in pre-cleaned containers that are of sufficient size for sample content as described above. All sample jars used are ordered as pre-cleaned and QA/QC grade. If jars are not pre-cleaned and QA/QC grade, then they will be reagent grade acetone and hexane rinsed before use. After the jars have been dried they will be sealed and stored until needed.

3.6.2 Weight Measurements

Crop samples will be weighed individually before compositing and the number and amount of material that furnished the composite sample per garden location will be recorded

3.6.3 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PCDD/F congeners as if it were an actual sample. Field blanks will be submitted at a rate of five percent of the total number of crop samples in accordance with US EPA recommendations. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for garden crop samples will consist of tissue homogenates from the garden crops collected spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8- TCDF.

3.7 Sample Packaging

After sample processing, each sample will be individually stored in chemically clean glass containers. The sample identification label will be taped to the outside of each container, each container will be placed into a waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual samples for the same species from the sample location will be kept together (if possible) in one large waterproof plastic bag in the same shipping container (ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

3.8 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed.

Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours. If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer unit will be used for temporary storage of garden crop samples and remaining tissue at the interim preparation facility location. Long-term storage of additional tissue or samples (until study termination) will take place at a storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University or an equivalent facility where they will be stored at –20°C until homogenization. All samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures previously specified.

3.9 Sample Shipping to Processing Facility

The various tissue samples will be hand-delivered or shipped to the processing location as soon as possible after collection and initial field processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples collected will be transported within 48 hours for processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there

will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

4.0 FINAL SAMPLE PREPARATION AND SHIPPING

4.1 Sample Receipt and Chain-of-Custody

Garden crop samples will be shipped or hand-carried from the field and delivered to a processing location for further sample processing. Sample processing and distribution for analysis ideally will be performed by one processing location. Transportation of samples from the field will be coordinated between the sampling team supervisor and the supervisor responsible for sample processing and distribution. An accurate written custody record will be maintained so that possession and treatment of each sample can be traced from the time of collection through analysis and final disposition.

Garden crop samples will be brought (or shipped) to the sample processing location in sealed containers accompanied by a copy of the sample request form, a chain-of-custody form, and the field records. Each time custody of a sample or set of samples is transferred; the Personnel Custody Record of the COC form will be completed and signed by both parties. Corrections to the COC form will be made in indelible ink by drawing a single line through the original entry, entering the correct information and the reason for the change, and initialing and dating the correction. The original entry should never be obscured.

When custody is transferred from the field to the sample processing location, the following procedure will be used:

• Shipping time will be noted (has the shipping time exceeded the appropriate time for preservation method used?).
• Check that each shipping container has arrived undamaged and that the seals are intact.
• Open each shipping container and remove the copy of the sample request form, the COC form, and the field records.
• Note the general condition of the shipping container (samples iced properly with no leaks, etc.) and the accompanying documentation (dry, legible, etc.).
• Locate individual samples listed on the COC form and note the condition of their packaging. Individual specimens should be properly wrapped and labeled. Note any problems (container broken, illegible labels, etc.) on the COC form.
• If individual samples are packaged together, check the contents of each composite sample container against the field record for that sample to ensure that the individual specimens are properly packed and labeled. Note any discrepancies or missing information on the COC form.
• Initial the COC form and record the date and time of sample receipt.
• Enter the following information for each composite sample into a permanent laboratory record book and, if applicable, a computerized database:

1 Sample identification number (specify conventions for specimen number)
2 Receipt date (YYYYMMDD)
3 Sampling date (YYYYMMDD)

4 Sampling site (name and/or identification number)
5 Garden crop (scientific name or code number)
6 Weight of sample

• If samples have been shipped on wet or blue ice, distribute them immediately to the technician responsible for sample preparation. If samples have been shipped on dry ice, they may be distributed immediately to the technician for processing or stored in a freezer at -20^{o} C for later processing. Once processed, samples should be stored according to the procedures described below.

4.2 Sample Processing

A. Garden crop samples received by the processing location will be stored at –20°C until they are ready for homogenization. Replicate samples or samples not immediately needed for sampling will be stored under the same conditions.

B. To ensure even distribution of contaminants throughout the samples and to facilitate extraction and digestion of samples, the garden crop samples will be ground and homogenized prior to being sent to the analytical laboratory for analysis. Previously cubed garden crop samples will be ground and homogenized in stainless steel blenders. Grinding and homogenization of tissue may be easier when it is partially frozen. Chilling the grinder/blender briefly with a few chips of dry ice may also help keep the tissue from sticking to it. The garden crop sample will be ground until it appears to be homogeneous. The ground sample should then be divided into quarters, opposite quarters mixed together by hand, and the two halves mixed together. The grinding, quartering, and hand-mixing steps should be repeated at least two more times. If chunks of tissue are present at this point, the grinding and homogenization will be repeated.

The preparation of each individual homogenate will be noted on the sample processing record. At this time, individual homogenates may be frozen separately. The sample processing location will prepare aliquots of the individual homogenates for analysis, distribute the aliquots to the appropriate laboratory, and archive the remainder of each homogenate along with the remaining tissue. Before, during, and after sample preparation, blenders will be washed with Liquinox soap, rinsed three times with distilled water, and reagent grade acetone and hexane rinsed. Other equipment and surfaces that may potentially contact the sample will be likewise cleaned regularly. Verification of the efficacy of cleaning procedures may be documented through the analysis of processing blanks or rinsates.

C. Homogenates will be aliquoted into four to six separate chemically clean I-CHEM jars according to the amount of the sample. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived. Remaining homogenates will be labeled and stored frozen. Sample IDs will be labeled for each replicate homogenate sample as described above.

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

The actual sample size required will depend on the analytical method used and the laboratory performing the analysis. Therefore, the exact sample size required for each type of analysis will be determined in advance with the analytical laboratory selected. The frozen aliquot(s) will be transferred on dry ice to the analytical laboratory accompanied by a sample transfer record. The sample transfer record will include a section that serves as the analytical laboratory COC record. The COC record will be signed each time the samples change hands for preparation and analysis.

Care will be taken during sample processing to avoid contaminating samples. This may be particularly problematic for PCDD/Fs, given the low levels that are of potential concern. Potential sources of contamination include dust, instruments, utensils, work surfaces, and containers that may contact the samples. All sample processing will be done in an appropriate laboratory facility under clean room conditions. Clean rooms or work areas will be free of organic contaminants. Periodic wipe tests may be conducted in clean areas to verify the absence of significant levels of organic contaminants. All instruments, work surfaces, and containers used to process samples will be of materials that can be cleaned easily.

4.3 Sample Shipping to Analytical Laboratory

Tissue homogenates, field blanks, and MS/MSD samples will be packaged and shipped for laboratory analysis according to US EPA/REAC guidelines (US EPA, 1994) as noted above.

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Samples will be transported to the analytical laboratory as soon as feasible after processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors

wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the analytical laboratory unless prior plans for such a delivery have been agreed upon with the laboratory staff. The time the samples were collected and time of their arrival at the analytical laboratory will be recorded on the COC form.

4.4 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD/Fs detected across sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, date and time of sample collection, sample and tissue type, lipid content of tissues, and PCDD/F concentrations of tissues. The data entry will be verified to ensure the accuracy of the information. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

4.5 Data Analysis

The objective of data analysis is to identify and report the PCDD/F concentrations measured in garden crops that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error), and develop a valid PDF for use in exposure and risk assessment. These steps will be outlined in the Exposure Assessment Work Plan. Ultimately, this information will be used to calculate the potential risk of PCDD/F exposure to humans through this pathway.

5.0 References

Blasland, Bouck & Lee. 1999. Sampling and Analysis Plan/Data Collection and Analysis Quality Assurance Plan. Blasland, Bouck & Lee, Inc., Syracuse, NY.

US EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - US EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

Stationary Airborne Agricultural Dust Study Plan

STUDY OBJECTIVES

The objectives of this work plan are:

1. To identify active farmland along the Tittabawassee River that may generate airborne dusts through normal and expected farming practices.
2. To locate stationary dust samplers on adjacent properties that represent actual or potential residential properties and receptors.
3. To collect repeated dust (total and respirable) samples at time intervals representing plowing, growing, harvesting, and fallow conditions
4. To submit these samples to a qualified analytical laboratory for polychlorinated dibenzo-p-pdioxin and polychlorinated dibenzofuran (PCDD/F) analysis.

The Study Plan presented herein is based on a review of available dust sampling methodologies and on an evaluation of conditions and agricultural activities within the Study Area. This Study Plan is based on analytical data needs for an assessment of human health risks via agriculturally generated airborne dusts in the Study Area. For this reason, the sampling procedures and data quality objectives may differ from customary sampling practices. All work planned and decisions made will be conducted in cooperation with the Michigan Department of Environmental Quality (MDEQ).

1.0 INTRODUCTION

Significant dust clouds caused by plowing and tilling as well as during harvest have been reported in the Study Area. The amount of PCDD/F residue adhering to the airborne dust particles released is unknown since not all agricultural soil disturbed is contaminated nor is all dust observed actually soil (much of it may be plant material).

Because this represents a potentially completed exposure pathway along the river, the Study will assess airborne dusts generated through farming activities along the Tittabawassee River or through simple wind erosion of agricultural land. In conjunction with other ongoing efforts to collect site-specific environmental data to assess exposure, this Study is designed to determine whether or not airborne dusts generated from typical farm activities present a completed exposure pathway for individuals who reside adjacent to active farming operations along the Tittabawassee River.

This Study Plan establishes guidelines and requirements for conducting the Stationary Airborne Dust Investigation for Tittabawassee River Farms (hereafter referred to as "this Study"). This Study has been developed in conjunction with a similar plan entitled *Personal Airborne Dust Exposure Study Plan.*

2.0 BACKGROUND

2.1 Study Area Location

The Study Area is located downstream of Midland, Michigan to the confluence of the Tittabawassee River with the Saginaw River. Along the Tittabawassee River are agricultural, residential and industrial lands. The Study Area experiences a continental climate with average temperatures ranging from 0º to 95º F. The average annual precipitation totals 33 inches of rainfall and 44 inches of snowfall. The mean relative humidity is 73% to 83%.

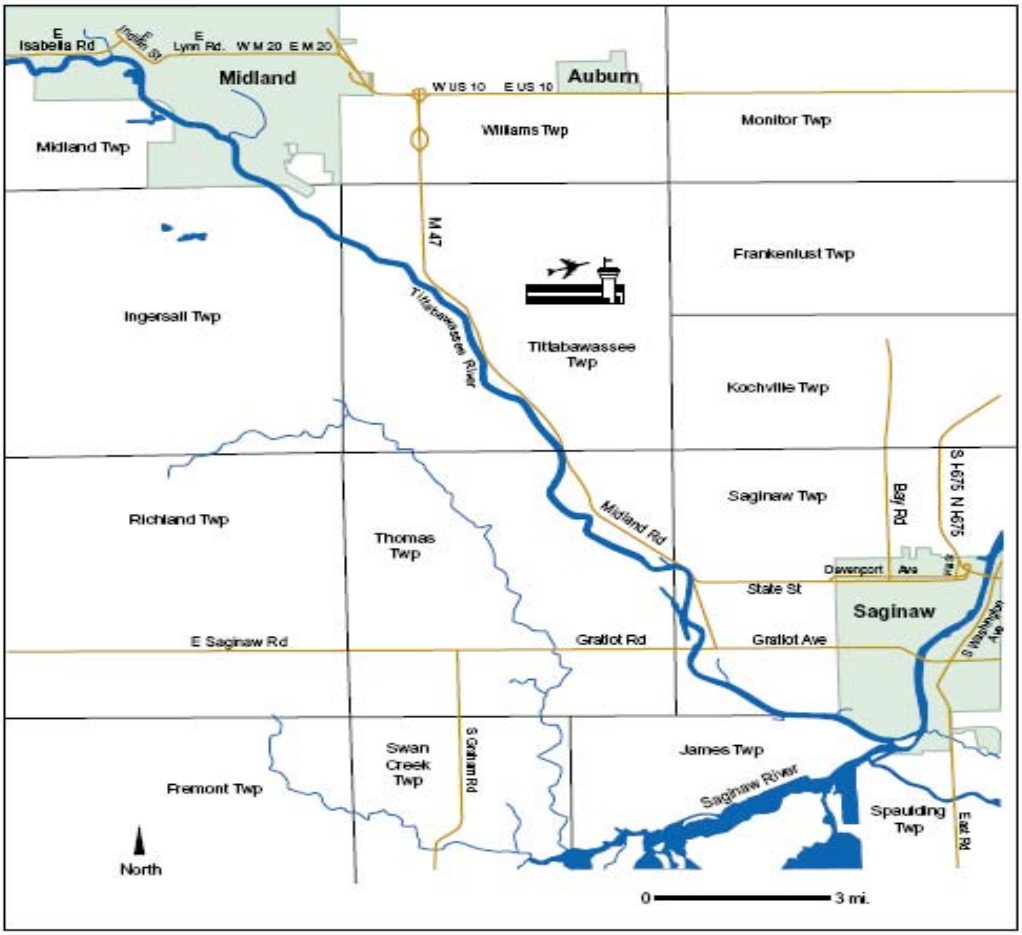
All Study Area investigations will be performed adjacent to farm property areas located along Tittabawassee River (**Figure 1**). Sampling will be conducted on residential properties (or properties that may become residential) next to active farming operations subject to existence and access. Dust samplers will be located next to houses or at the closest location that a house could exist based on local construction ordinances and the availability of power. The data obtained from these studies is intended to represent potential inhalation exposure of residents who live in proximity to agricultural areas along the Tittabawassee River. These inhalation exposures will address potential exterior dust exposure associated with tilling, harvesting, other time periods as well as potential wind erosion.

2.2 Sampling Locations

For the purposes of this study, all sampling locations will be selected from farms located along the Tittabawassee River. Primarily these farms will consist of a well-delineated, active farm area that includes tilled pasture or fields. Representative farms will be selected based on their location within the Study Area and the type of farming operation in consultation with the Michigan Department of Environmental Quality (MDEQ). Other sources of information on farming along the river will be gathered from the Michigan Department of Agriculture (MDA), local extension agents and the planned Activity Survey. Selection preference will be for farms that till and harvest crops in a manner that the potential for dust generation exists and which are adjacent to developed residential property.

For purposes of this study, five farms that have adjacent residential properties will be located and, if available, selected for airborne dust sampling during this project in consultation with MDEQ. An additional farm located upstream of Midland will be selected to collect background dust data for comparison purposes.

Figure 1. Map of Tittabawassee River Study Area



3.0 SCOPE OF WORK

This document provides the Study Plan protocols for the collection of airborne agricultural dust samples for subsequent analysis for the presence of PCDD/Fs and the identification of sources and activities within the sampled area that may contribute to the observed results. Protocols will be provided for stationary sampling of airborne dusts adjacent to study farms.

Sampling procedures may be varied or changed as necessary, dependent upon site conditions, equipment limitations, or limitations imposed by access, by the procedure or agricultural practices, and in conjunction with MDEQ and MDA approval. In all instances, the final procedures employed will be documented and reported in the final report.

4.0 STUDY AREA SAMPLING ACTIVITIES

The following section describes Study Area-specific sampling and analysis activities. A summary of the proposed sampling and analysis requirements is provided in **Table 1**. Data quality objectives are described in **Section 6.**

4.1 Stationary Air Samples

Five to ten stationary air samplers equipped with two-stage cyclonic dust impacters (or an equivalent particulate sampler) will be located adjacent to cultivated fields next to residences or in areas where residences could be located (1 to 2 per residential property). Dust samples collected from each Study Area farm for a specific duration at regular intervals throughout the duration of this project. In total, 50 to 100 stationary airborne dust samples will be collected for this project. Parameters such as distance from the farm field, tree line barriers separating the farm field from the residence, or other landscape features of note that could influence agricultural dust migration to the residence will be recorded.

4.2 Target Analyte Selection

The primary focus of this sampling effort is to determine the concentrations, patterns, and variability of polychlorinated dioxins and furans (PCDD/Fs) in agriculturally generated airborne dust collected along the Tittabawassee River.

4.3 Sampling Preparation

The primary purpose of this sampling is to collect sufficient airborne dust from the agricultural soils disturbed by farming activities or wind to determine the concentration of congener-specific PCDD/Fs in collected dust samples. If sample size is sufficient, a split of the dust sample will be retained to allow duplicate or split analysis if needed. Airborne dusts will be collected at various agricultural and residential locations along the Tittabawassee River and will be collected just prior to, during, and after planting and harvest as well as other periods during the year, so that the sampling effort will represent both normal and peak dust generating activities. MDEQ will be notified of sampling dates and locations prior to actual dust sampling.

Safety training requirements are consistent among all protocols for field studies, and will be developed for this effort. Dust sample collection activities will be initiated only after the dust sampling work plan is approved by MDEQ. This section details the overall sampling methodology, equipment and techniques to be employed in the dust sampling effort, considerations for ensuring preservation of

sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation, and shipping. All practices will be conducted in such a way to maximize public safety.

For each airborne dust samples collected, the following field observations and measurements will be recorded:

- Sample ID
- Location (including distance between farm field and residence as well as other landscape features of significance, if any)
- Weather, wind direction, and farming activities
- General site description
- Photographs
- GPS coordinates
- Start and end date and time of sampling
- Collectors initials

After recording observations and measurements, the dust sample will be processed as described below.

4.4 Sampling Equipment and Use

The project team will assemble and pack all equipment specified below in advance of the dust-sampling event. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample material and containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

The field equipment and supplies needed for agricultural dust sample collection may include:

- SOP for dust sampling
- Site Health and Safety Plan
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Detailed maps of sampling site locations
- Pencils/Pens
- Sharpie waterproof markers
- Waterproof field notebook and clipboard
- Field Sampling Checklist
- Chain of custody (COC) forms
- Field data documentation forms

- Sample labels and sample tags
- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- 2-way radio and/or cell phone
- GPS receiver
- Digital camera
- High Volume Air Samplers
- Calibration Equipment
- Filter Material
- Two (or more) stage cyclonic impacters
- Extension cords
- Duct tape
- Garbage bags
- Packing tape
- String
- Field thermometer
- Several sizes of plastic bags for holding individual samples
- Aluminum foil (extra heavy duty)
- Gloves
- Rain gear
- Coolers
- Ice (wet ice, blue ice packets, or dry ice)
- Filament-reinforced tape to seal ice chests for transport to laboratory
- Sample preservation and shipping supplies

4.5 Sampling Regime

Sampling will occur over a 12 month period with particular focus on the planting (spring) and harvest (fall) season. Sampling during the summer and winter will take place to reflect crop growing periods and fallow conditions when agricultural dust should be at a minimum. Sampling will be conducted in two one-week periods in the month prior to, during, and after these seasons. These sample events may be a single weeklong event or divided into 24-hour sampling events dependent on the dust loads encountered. In either case, the sampling period and volume of air sampled will be recorded for purposes of estimating an airborne dust concentration associated with framing activities and normal wind erosion. Additionally, a weeklong dust sample event will also occur at mid-summer and mid-winter. Samples will be collected from each sample location based on the Sample Matrix presented in **Table 1**, below. This Sampling Matrix will be applied to each Study farm for the duration of this study.

Table 1. Sample Matrix for Residential Property Adjacent to a Study Farm

Sample Time (Sample Duration)	Stationary Dust Samples/Sampler	Total
Pre-Planting (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Planting (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Post-Planting (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Mid-Summer (One Week)	1 weeklong sample or 1 set of 5 daily samples (composited)	1 to 2 samples
Pre-Harvest (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Harvest (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Post Harvest (Two Weeks)	2 weeklong samples or 2 sets of 5 daily samples (composited)	2 to 4 samples
Mid-Winter (One week)	1 weeklong sample or 1 set of 5 daily samples (composited)	1 to 2 sample
Total Samples[1]		22 to 44 samples

[1]Sample totals do not include duplicates, field blanks, or matrix spike samples.

4.6 Sampling Procedure

This section details the overall sampling methodology, equipment, and techniques to be employed in the agricultural dust sampling.

A. High volume dust samplers will be equipped with pre-weighed particulate filters that allow separation of respirable and non-respirable particulates. The dust samplers will be calibrated and located on residential property or property that may be residential in the future. Sampling will be carried out in 24 hour or weeklong increments selected as to not overload the dust sampler at intervals described in **Table 1**. Dust samples will be collected by standard practices or modified according to need as decided in conjunction with MDEQ.

B. After a sampling period is complete, the location of each sampler will be recorded with coordinates from a global positioning system (GPS). The condition of the sampler, the filter material, and other relevant environmental parameters, such as time, temperature, or wind direction, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. The filter material will be removed and tagged with pre-printed labels. One sample label will be attached to the filter container and one sample label will be attached to the bag in which the filter material is placed.

D. Digital photographs will be taken of the sampler and filter and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, start and end date and time, and collector initials.

F. After reloading the dust sampler with new filter material, re-calibrating the devices and noting the new sampling date, the used filter material will be placed in an appropriate collection bag or container, and the sample will be transported to an interim facility for packing and shipping.

G. Before shipping, dust filters will be weighed to the nearest gram. The information will be recorded in the appropriate field laboratory notebook.

H. All surfaces and instruments that might contact the dust samples will be rinsed with reagent grade acetone or hexane before and after filters are handled.

I. If sufficient dust is collected, a split of the sample will be retained for additional analysis, if needed.

J. Dust filter samples will be placed in pre-labeled, chemically clean I-CHEM jars or other appropriate shipping containers, and will be immediately placed on ice and shipped to the laboratory. Any duplicate or split samples will be similarly preserved and shipped.

4.7 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is preserved by prevention of loss of contaminants already present in the dust and prevention of extraneous contamination.

All potential sources of contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. Ice chests will be scrubbed clean with detergent and rinsed with distilled water after each use to prevent contamination. To avoid contamination from melting ice, samples will be placed in waterproof plastic bags. Sampling equipment that has obviously been contaminated will be cleaned or not be used. All equipment that will be used directly in handling dust samples will be cleaned prior to each sampling trip, rinsed in acetone and pesticide-grade hexane, and stored in aluminum foil until used. Between sites, the field collection team will clean any preparation surfaces by rinsing them with acetone and hexane and mopping with bleach at the end of the sampling period or as necessary.

Ideally, all processing of collected dust after it is removed from the air sampler will be performed under clean room conditions to reduce the possibility of sample contamination. If additional sample preparation must be performed in the field, a clean area will be set up away from sources of contamination to help reduce the potential for inadvertent surface and airborne contamination of the samples. If sample processing is conducted in the field, a notation will be made in the field records and on the sample processing record.

4.8 Field Recordkeeping

Thorough documentation of all field sample collection and processing activities is necessary for proper interpretation of dust sampling results. The data collection phase includes the completion of a various sample-tracking forms, which includes information regarding the sample collection procedures. The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel will be properly trained in these areas and perform these tasks in secured access facilities.

Field personnel will document all sampling activities in accordance with the Work Plan. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing laboratory. These are 1) Field record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection and (b) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

4.8.1 Field Record Form

For each individual dust sample that is collected, the following observations and measurements will be recorded at a minimum:

- Sampler Number
- Start and end date and time collected
- Volume of air sampled
- Pre and post calibration information
- Temperature and weather conditions
- Site location and GPS coordinates
- Pre and post weight of filter
- Collectors name(s) and signatures

- Affiliation (including telephone number and address)

An example field record form is provided in Appendix A.

4.8.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format.

Samples shall be labeled with a unique number designated with a letter code for sample type followed by a six-digit designation of the day, month and year the sample was collected. This will be followed by the Study Area-specific sample location number and a running number for that site. Sample types should be identified as follows:

SAS–Stationary Air Sample

For example: **SAS031506-01-01** is the first stationary air sample collected on March 15, 2006 from sample location No. 1.

Quality Assurance/Quality Control samples should be designated in the same manner as above with no modification. Spikes and double spikes will be submitted to the laboratory as a blind. Sample type and numbers will be recorded on the field sample forms.

A completed sample identification label will be taped to each container and the individual filter sample will be placed in a waterproof plastic bag.

4.8.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual Dust sample. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling start and end date/time
- Processing and analysis requested

- Preservation method (wet/dry ice)

After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual sample. Information on the COC label will also be recorded on the COC form.

4.8.4 Chain-of-Custody Form

Dust samples collected for analysis will be tracked in the field and in transit to the processing laboratory and then to the analytical laboratory. Individual sample containers will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g.*, ice chest) used. All pertinent information will be entered into the chain-of-custody form in the field including in-transit and laboratory delivery relinquishment or receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for analysis; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight, or locked in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

4.8.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, weather conditions, equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the dust sample data. This will also include method of sampling, air volume sampled, calibration data, start time, ending time, sampling duration, sampling location, and sampling conditions.

5.0 DATA QUALITY OBJECTIVES

Data Quality Objectives (DQOs) guide data collection and analysis to ensure that data are of adequate quality and sufficient quantity to support decision-making for evaluating human health concerns. DQOs are determined by the anticipated end uses of the data to be collected. In accordance with US EPA policy, DQOs should be developed for each data collection activity.

The DQOs for collection of dust samples are as follows:

- determine the concentration of PCDD/Fs in the airborne dusts and compare these levels to human health benchmark concentrations, risk-based levels, or background levels as appropriate, based on project objectives.

- Obtain the necessary data to characterize the potential hazard to human health from exposure to these dusts through inhalation.

All samples that are collected are to be used to provide data on Study Area characterization, human health and safety, and baseline data for continued monitoring or evaluation.

5.1 Analytical Support Level

Analytical data generated under this Work Plan should be consistent with the data collection and risk assessment (US EPA analytical support Level III to V) when sampling contaminated media at human exposure points. Unless otherwise specified, laboratory analysis of all environmental and Quality Assurance/Quality Control (QA/QC) samples should be of Level IV. As specified in Level IV criteria, only approved US EPA analytical methods should be used corresponding to current Contract Laboratory Program (CLP) or SW-846 methodology.

5.2 PARCC

Data quality assessment parameters of precision, accuracy, representativeness, completeness, and comparability (PARCC) should be specified to establish acceptance criteria for all analytical data. These DQOs are expressed as quantitative and qualitative statements concerning the type of data needed to support a decision based on a specified level of uncertainty.

5.2.1 Precision

Precision is a measure of mutual agreement among replicate (or between duplicate) or co-located sample measurements of the same analyte. The closer the numerical values of the measurements are to each other, the more precise the measurement. Precision is determined by the spread of data about their mean. The spread presents how different the individual reported values are from the average reported value. Precision is thus a measure of the magnitude of errors, and should be expressed as the relative percent difference (RPD) between the analyte in a sample and associated duplicates.
This quantity is defined as follows:

$$RPD\ (\%) = 100 \times \frac{|S - D|}{(S + D)/2}$$

where: S = concentration of an analyte in a sample
D = concentration of an analyte in a duplicate sample

In addition, precision should be maintained by conducting routine instrument checks to demonstrate that operating characteristics are within predetermined limits.

5.2.2 Accuracy

Accuracy is a measure of bias in a measurement system. The closer the value of the measurement agrees with the true value, the more accurate the measurement. This should be expressed as the percent recovery of an analyte from a surrogate, matrix spike, or standard reference sample. These samples, having known analyte concentrations, should be analyzed in the laboratory for comparison.

Accuracy measures the average or systematic error of an analytical method. This measure is defined as the difference between the average of reported values and the actual value. Accuracy should be expressed as the percent bias. The closer the value is to zero, the more accurate the data. This quantity is defined as follows:

$$Bias\ (\%) = \frac{MC - KC}{KC} \times 100$$

where: KC = known concentration of an analyte
MC = measured concentration of an analyte

5.2.3 Representativeness

Representativeness is a qualitative parameter that expresses the degree to which sample data accurately and precisely represents a characteristic of a population, parameter variations at a point, or an environmental condition. The design and rationale for the sampling program previously described ensures that the environmental conditions present in the Study Area should be sufficiently representative.

5.2.4 Completeness

Completeness is a measure of the number of valid measurements obtained in relation to the total number of measurements planned. The closer the numbers are, the more complete the measurement process. Completeness should be expressed as the percentage of valid to planned measurements and is calculated as follows:

$$\text{Completeness (\%)} = \frac{V}{P} \times 100$$

where: V = number of valid measurements
P = number of planned measurements

5.2.5 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared to another. Data sets should be compared only when precision and accuracy meet the specified acceptance criteria. Sample data should be collected and reported in order to be comparable with other measurement data for similar samples. Comparability should be maintained through consistency in sampling conditions, selection of sampling procedures, analytical methods, and data reporting units. The US EPA CLP or SW-846 analytical methods selected for this investigation should be commensurate with those from previous investigations at the Study Area to assure comparability with other data sets.

5.3 Quality Control Checks

Quality control checks of both field sampling and laboratory sample analysis should be used to assess and document data quality. The collection and analysis of the quality control samples described below should be used for this purpose. Results from these quality control samples should be employed to determine the precision of sample collection and handling procedures, the accuracy of the laboratory analysis, the thoroughness of field equipment decontamination procedures, and the representativeness of the environmental samples.

5.3.1 Field Duplicates/Replicates

Field duplicates (or replicates) may be collected at selected locations to evaluate the environmental variability at a location and the precision of laboratory measurement if it is determined that such a need and sufficient sample quantity exists. Field duplicates can be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping although field blanks may suffice in this complicated sampling. If needed, field duplicate samples should be provided to meet US EPA's recommendation that such samples should be submitted at a rate of five to ten percent of the total number of samples.

5.3.2 Field Blanks

Field blanks should be used to indicate the presence of external contaminants that may have been introduced into the samples during the collection, transport and analytical processes. Field blanks will be prepared in the Study Area during the sampling event. A field blank will consist of clean, unused filter material that is prepared, stored, and analyzed for PCDD/PCDF congeners as if it were an actual sample. These samples will be handled in the same manner as those used in the actual sampling of the Study Area. At least one field blank will be analyzed for each sampling event.

5.3.3 Matrix Spike/Matrix Spike Duplicates

In addition to the control samples identified below, the laboratory should use a series of control samples as specified by the CLP or SW-846 method. These include a method blank, surrogate, matrix spike, and matrix spike duplicate. Two additional dust samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. Matrix spike/matrix spike duplicates (MS/MSD) should be prepared and analyzed for selected samples at a minimum of five percent of the total number of environmental samples collected for each matrix. The matrix spikes for dust samples will consist of dust from samples collected spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8- TCDF. Analysis of these duplicate samples should be performed for samples of similar matrix type and concentration, and for each sample batch (sample delivery group) of no more than 20 samples. Quality control samples should be handled and analyzed in the same manner as all environmental samples.

In general, MS/MSD samples will be prepared by the laboratory, identification and the concentrations will be based on the estimated concentration of

contaminants, and the characteristics of each matrix. Field personnel will introduce spikes as blind samples for analysis.

5.3.4 Reporting Limits

Data quality needs are met by the CLP contract required detection limits (CRQLs), or the SW-846 method detection limit for each analyte. At a minimum, detection limits must be below the potential safe human levels applied to the data. The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of the target analytes in dust samples from disturbed agricultural soils at various locations along the Tittabawassee River. In the case of congener-specific PCDD/Fs analyses, the detection limit selected is generally in the range of 0.1 part per trillion (ppt) in view of the likely amount of dust available for analysis. Non-detects will be handled as Limit of Detection (LOD) = 0.

The detection limits specified in the US EPA analytical methods for this study satisfy the DQOs for this investigation. The use of standard sampling methods, US EPA analytical methods, and data validation ensures that detection limits will be useful for conducting assessments of public health, and comparable to previous studies.

5.3.5 Data Validation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD/F detected in dust samples across sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, calibration, start and end date and time of sample collection, sample type, and PCDD/F concentrations in the agricultural dust sample. The data entry will be verified to ensure the accuracy of the information.

All decisions and recommendations should be based upon validated analytical data. All analytical data generated by the laboratory should be validated in accordance with the quality control criteria specified in the US EPA CLP statements of work. The purpose of the validation process is to eliminate unacceptable analytical data, and to designate a data qualifier for any data quality limitation discovered. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination. An assessment of data usability should determine the degree to which validated data are suitable for the purposes intended, and whether the data are useful for other purposes.

5.3.6 Data Analysis

The objective of data analysis is to identify and report the PCDD/F concentrations measured in dust samples that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error), and develop a valid PDF for use in exposure and risk assessment. These steps are outlined in the Exposure Assessment Work Plan. Ultimately, this information will be used to calculate the potential risk of PCDD/F exposure to humans.

6.0 DATA COLLECTION METHODOLOGY

6.1 Stationary Air Sampling

Study Area personnel should maintain field notes on sample form (Appendix A – Field Sample Form). Information included in the field sample forms will consist of calibration data, weather and other environmental parameters, sample numbers and designations, location, time in the Study Area, personnel and equipment present, down time, materials used, and any other pertinent information necessary to reconstruct field activities at a later date.

6.1.1 Stationary Air Sampling Procedures and Equipment

All high volume dust sampling pumps will be calibrated prior to use at the Study Area. The pumps shall be calibrated for maximum rate in L/min that the dust sampling media will support. It is assumed that standard high volume air samplers will be employed and that they will be equipped with a two (or more) stage cyclonic impacter to allow respirable dusts to be separated from the total particulate load. All materials used in sample collection will be cleaned prior to use. On arrival at the Study Area, sampling personnel shall place all air sampling pumps such that the collection orifice is approximately 1 meter off the ground and the orifice is free of any obvious obstructions to air flow. All pumps will be controlled by timers set to start at the beginning of the sample period and end at the pre-selected end of the sampling period (a minimum of 24 hours and a maximum of 120 hours depending on the dust load encountered). Throughout the sampling period, sampling personnel shall periodically inspect the samplers to ensure that they are operating correctly and that no filter clogging has occurred.

At the end of the sampling period, the filter apparatus shall be sealed. Volume of air sampled and time sampled will be recorded for each individual sample, even those that may be composited later. Post calibration shall be conducted using the field sample. All final samples will be placed in secondary, labeled, and separate containers to protect the sample during transport to the analytical laboratory.

All sampling, calibration, data collection and documentation will be conducted under supervision.

6.2 Sample Containers and Handling

After sample processing, each filter sample, blank or duplicate will be individually stored in chemically clean glass containers. The sample identification label will be taped to the outside of each container, each container will be placed into a

waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual samples from the same locations will be kept together (if possible) in one large waterproof plastic bag in the same shipping container (ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

Sample transport containers should be affixed with a sample label that should be filled out at the time of collection. Information on the sample label should include, at a minimum, the following: (1) Study Area location, (2) sample numbers, (3) date and time of sample, (4) initials of sampler, and (5) parameters to be analyzed. Chain-of-custody forms should be initiated at the time of collection by the sampler.

6.3 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed. Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours. If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer unit may be used for temporary storage of dust samples. Long-term storage of remaining samples (until study termination) will take place at an off-site storage location yet to be determined. Dust filter samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University, or an equivalent facility, where they will be stored at –20°C until shipped. All samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified above.

6.4 Sample Shipping to Laboratory

The dust samples will be hand-delivered or shipped to the analytical laboratory as soon as possible after collection and initial processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed may include:

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms

- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Dust filter samples will be transported to the laboratory within 48 hours for processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there may be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

7.0 DECONTAMINATION/INVESTIGATION-DERIVED WASTES

Applicable decontamination and waste handling procedures are addressed in this section.

7.1 Decontamination

Due to the nature of the material to be sampled, a centralized decontamination area is not deemed necessary for this Study Area. Appropriate cleansing of preparation areas to prevent cross contamination has been previously discussed.

7.2 Investigation - Derived Waste Collection and Storage

Anticipated solid wastes from this sampling activity include latex gloves and sample labeling materials. A designated waste bag will be established for stockpiling and storage of these materials. Study Area personnel will be responsible for final disposal of the waste.

8.0 REFERENCES

American Society For Testing And Materials, Standard Test Method for Particle Size Analysis of Soils, Designation D 422-63, Reprinted from the Annual Book of ASTM Standards, Philadelphia, PA.

Environmental Protection Agency and Michigan State University. (2005). Dioxin contamination and the Tittabawassee River and Floodplain. Managing the risks: An issue guide.
http://www.nifi.org/stream_document.aspx?rID=3926&catID=15&itemID=3925&typeID=8

Saginaw County Chamber of Commerce. (2006). Relocation information. Website visited on 3/21/06. http://www.saginawchamber.org/Chamber/facts1.htm

U.S. Census Bureau. (2001). Census 2000: Table DP-1. Profile of General Demographic Characteristics. Geographic area: Saginaw County, Michigan.
http://censtats.census.gov/data/MI/0602614579840.pdf

US Department of Agriculture. (2003). 2002 Census of Agriculture county profile: Saginaw, MI.
http://www.nass.usda.gov/census/census02/profiles/mi/cp26145.PDF

US Environmental Protection Agency. (2006). Saginaw River/Bay Area of Concern. Website visited on 3/21/06. http://www.epa.gov/glnpo/aoc/sagrivr.html

Appendix A - Sampling Form

LOCATION: _____ **DATE:** _____ **Pg.** _____ **of** _____

ADDRESS: _____ **SITE REF. #:** _____

_____

AREA/WORKPLACE: _____

WORKER: _____ **SAMPLER:** _____

ID #: _____ **SHIFT:** _____ **BARAMETRIC PRESSURE:** _____

JOB TITLE: _____ **TEMP:** _____ **HUMIDITY:** _____

_____ **WIND SPEED:** _____ **DIRECTION:** _____

NOTES ON : TIME / TASK DESCRIPTION / EQUIPMENT AND PPE

PUMP S/N: _____

SAMPLE DATA	SAMPLE #:	SAMPLE #:	SAMPLE #:	SAMPLE #:
START TIME				
STOP TIME				
TOTAL TIME				
TYPE				
STRATEGY				
SUBSTANCE(S)				

PRE-CALIBRATION: **LOCATION:**_____

PUMP MFG:_____ **S/N:**_____

CAL. METHOD:_____ **DATE:**_____

CAL. BY:_____ **FLOW RATE:**_____

POST-CALIBRATION: **LOCATION:**_____

DATE:_____ **CAL. BY:**_____

FLOW RATE:_____ **AVE. FLOW RATE:**_____

CALCULATIONS

SAMPLE RESULTS **LAB. USED:**

SAMPLE #	SUBSTANCE(S) / SAMPLE METHOD(S)	TOTAL TIME	FLOW RATE	VOLUME	AIR. CONC	TWA $_8$	OEL

Personal Airborne Dust Exposure Study Plan

STUDY OBJECTIVES

The objectives of this work plan are:

1. To identify active farms along the Tittabawassee River that engage in activities that have the potential to generate airborne dusts.
2. To recruit farmers who work these properties to participate in collecting personal dust samples at different periods of the year.
3. To collect respirable dust samples using personal sampling pumps and two (or more) stage dust filters attached to these individuals.
4. To submit these dust samples to a qualified analytical laboratory for dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F) analysis.

The sampling and analysis guidelines and requirements presented herein are based on a review of available information and on an evaluation of potential exposures in the Study Area. This Study Plan is based on analytical data needs for an assessment of human health risks in the Study Area. For this reason, the sampling procedures and data quality objectives may differ from customary sampling practices. All work planned and decisions made will be conducted in cooperation with the Michigan Department of Environmental Quality (MDEQ).

1.0 INTRODUCTION

Significant dust clouds caused by plowing and tilling as well as during harvest have been reported. The amount of PCDD/F residue adhering to the airborne dust particles released is unknown since not all agricultural soil disturbed is contaminated nor is all dust observed actually soil (much of it may be plant material).

This study is intended to collect exposure data on farmers plowing the fields and harvesting the crops since regular farming activities that generate airborne dusts with these residues could result in elevated exposure to farmers. This Study is designed to determine whether or not airborne dusts generated from typical farm activities present a completed exposure pathway for individuals who work on farms along the Tittabawassee River and to quantify such exposures.

This work plan establishes guidelines and requirements for personnel during the conduct of this investigation and the sampling required to perform the Personal Airborne Dust Investigation (hereafter referred to as "the Study"). This work plan has been developed in conjunction with a separate plan entitled *Stationary Airborne Agricultural Dust Study Plan*.

2.0 BACKGROUND

2.1 Study Area Location

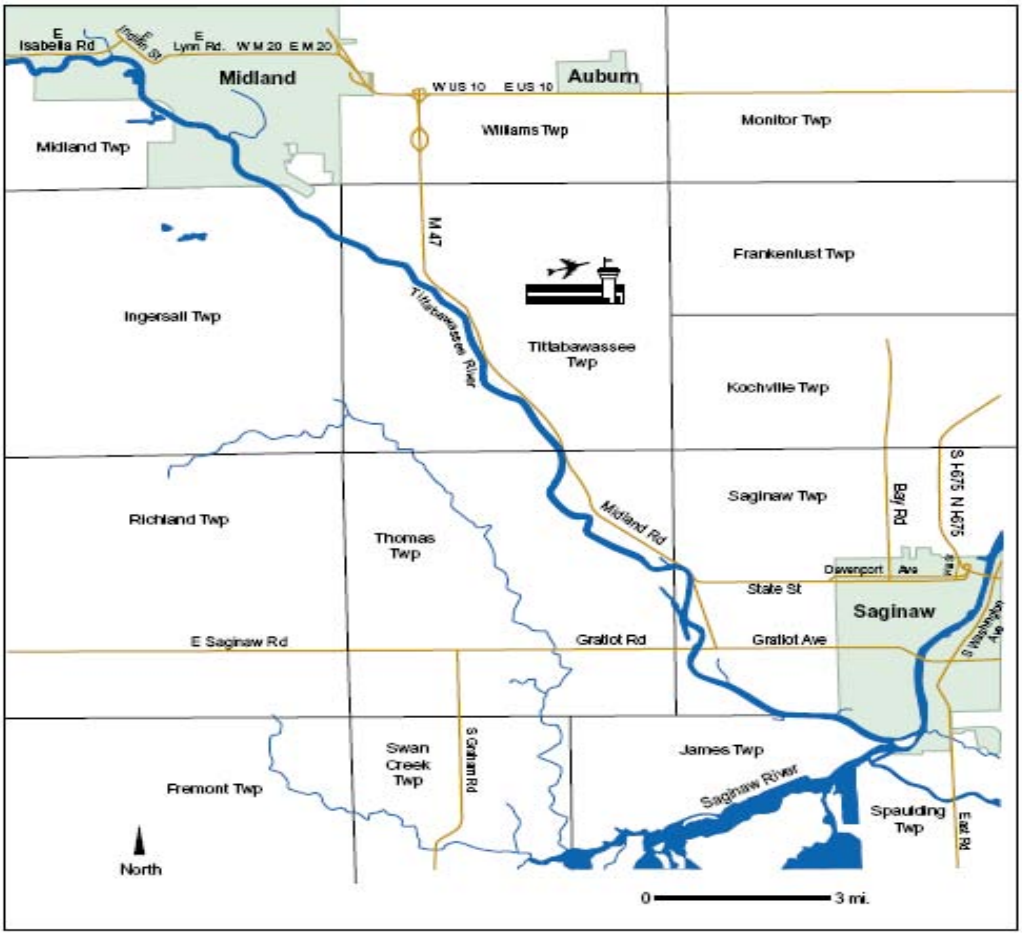
The Study Area is located downstream of Midland, Michigan to the confluence of the Tittabawassee River with the Saginaw River. Along the Tittabawassee River are agricultural, residential and industrial lands. The Study Area experiences a continental climate with average temperatures ranging from 0º to 95º F. The average annual precipitation totals 33 inches of rainfall and 44 inches of snowfall. The mean relative humidity is 73% to 83%.

2.2 Sampling Locations

For the purposes of this study, all sampling locations will be on Tittabawassee River farms. Primarily these farms will consist of a well-delineated, active farm area that includes tilled pasture or fields. Representative farms will be selected based on their location within the Study Area and the type of farming operation in consultation with the Michigan Department of Environmental Quality (MDEQ). Other sources of information on farming with the floodplain will be gathered from local extension agents and the planned Activity Survey. In order to properly explore the issue raised, selection preference will be for farms that till and harvest crops.

Information will be solicited from local farmers and extension agents as well as gathered from the planned site-specific Activity Survey. Once the number of farms is located, individual farmers will be approached and recruited for the project. Farmers who agree to participate will receive the results of their individual samples if requested. For initial planning purposes, up to ten farmers who meet the study requirements will be recruited for airborne dust sampling during this project in consultation with MDEQ. An additional two farmers working upstream of Midland will be selected to collect background personal dust data for comparison purposes.

Figure 1. Map of Tittabawassee River Study Area



3.0 SCOPE OF WORK

This document provides protocols for the collection of personal airborne dust samples for subsequent analysis for the presence of PCDD/F and the identification of sources and activities within the sampled area that may contribute to the observed results. Protocols will be provided for personal air monitoring of individuals who work at these farms and engage in farming activities that generate dust.

Sampling procedures may be varied or changed as necessary, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure or agricultural practices, and in conjunction with MDEQ. In all instances, the final procedures employed will be documented and reported in the final report.

4.0 STUDY AREA SAMPLING ACTIVITIES

The following section describes Study-specific sampling and analysis activities. A summary of the proposed sampling and analysis requirements is provided in **Table 1**. Data quality objectives are described in **Section 6.**

4.1 Personal Air Monitoring

Personal air-monitors equipped with two (or more) stage dust filters will be attached to farmers at the beginning of their workday. These samplers will be calibrated at the beginning and end of the sampling period so that the amount of air sampled per minute is known as well as the total amount of time the sample comprises. Samplers will be attached to the farmer's belt and the filter cassette clipped to his or her collar. A length of flexible tubing will be used to attach the filter cassette to the sampler. Respirable dust samples will be collected over the course of five days during periods of plowing (spring) and harvesting (fall) as well as a period in between (tilling) from each farmer in the Study. In total, approximately 170 personal dust samples will be collected for this project, although some from the same farmer/time period may be composited if appropriate.

4.2 Sampling Preparation

The primary purpose of this sampling is to collect sufficient airborne dust in the breathing zone of a farmer from the agricultural soils disturbed by farming to determine the concentration of congener-specific PCDD/Fs in said dusts. If sufficient sample quantity is available, dust will be retained to allow duplicate or split analysis if needed. Airborne dusts will be collected from personal air samplers attached to farmers working land along the Tittabawassee River floodplain and will be collected during planting and harvest as well as during normal crop maintenance, so that the personal sampling effort will represent both normal and peak dust generating activities. MDEQ will be notified of sampling dates and locations prior to actual dust sampling.

Safety training requirements are consistent among all protocols for field studies, and will be developed for this effort as well. Personal dust sample collection activities will be initiated only after the personal dust sampling work plan is approved by MDEQ. This section details the overall sampling methodology, equipment and techniques to be employed in the dust sampling effort, considerations for ensuring preservation of sample integrity, field recordkeeping, and chain-of-custody procedures associated with sample processing, preservation,

and shipping. All practices will be conducted in such a way to maximize public safety.

For each airborne dust samples collected, the following field observations and measurements will be recorded:

- Sample ID
- Location
- Weather, wind direction, and farming activities
- General site description
- Photographs
- GPS coordinates
- Start and end date and time of sampling
- Collectors initials

After recording observations and measurements, the dust sample will be processed as described below.

4.3 Sampling Equipment and Use

The project team will assemble and pack all equipment specified below in advance of the personal dust-sampling event. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample material and containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

The field equipment and supplies needed for personal dust sample collection may include:

- SOP for personal dust sampling
- Site Health and Safety Plan
- First aid kit (including emergency phone numbers of local hospitals, family contacts for each member of the sampling team)
- Detailed maps of sampling site locations
- Pencils/Pens
- Sharpie waterproof markers
- Waterproof field notebook and clipboard
- Field Sampling Checklist
- Chain of custody (COC) forms
- Field data documentation forms
- Sample labels and sample tags

- Re-sealable watertight plastic bags for storage of Field Records, COC Forms, and Sample Request Forms
- 2-way radio and/or cell phone
- GPS receiver
- Digital camera
- Personal Air Samplers
- Calibration Equipment
- Filter Cassettes
- Two (or more) stage impacters
- Duct tape
- Garbage bags
- Packing tape
- String
- Field thermometer
- Several sizes of plastic bags for holding individual samples
- Aluminum foil (extra heavy duty)
- Gloves
- Rain gear
- Coolers
- Ice (wet ice, blue ice packets, or dry ice)
- Filament-reinforced tape to seal ice chests for transport to laboratory
- Sample preservation and shipping supplies

4.4 Sampling Regime

All sampling will occur over an approximately 6 to 12 month period with particular focus on the planting and harvest season as noted. Sampling will be conducted in one-week (5 days) durations during these seasons. Samples will be collected from each farmer and location based on the Sample Matrix presented in **Table 1**, below. This Sampling Matrix will be applied to each Study farmer for the duration of this study.

Table 1. **Sample Matrix for a Study Farm**er

Sample Time (Sample Duration)	Personal Air Monitoring Samples	Sub Total
Planting (One Week)	One sample collected daily for five days	5 samples (1 composite)
Mid Summer (One Week)	One sample collected daily for five days	5 samples (1 composite)
Harvest (One Week)	One sample collected daily for five days	5 samples (1 composite)
Total Samples[1]		15 samples (3 composites)

4.5 Sampling Procedure

This section details the overall sampling methodology, equipment, and techniques to be employed in the agricultural dust sampling.

A. Fully charged personal air samplers will be equipped with pre-weighed particulate filters and impacters that allow separation of respirable and non-respirable particulates. The air samplers will be calibrated in the field at the beginning and end of each sampling period and attached to the belt of the participating farmer. The filter train will be attached to the collar in the breathing zone and the sampler attached to the filter with a length of flexible, inert tubing. Sampling will be carried out over the entire workday for a period of one week during plowing harvest and crop maintenance activities at intervals laid out in **Table 1**. Sample filters will be switched out if the dust threatens to overload the air pump. Personal dust samples will be collected by standard practices or modified according to need as decided in conjunction with MDEQ.

[1]Sample totals do not include duplicates, field blanks, or matrix spike samples.

B. After a sampling period is complete, the location of each farm and area worked will be recorded with coordinates from a global positioning system (GPS). The condition of the sampler, the filter material, and other relevant environmental parameters, such as time, temperature, or wind direction, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. The filter material will be removed and tagged with pre-printed labels. One sample label will be attached to the filter container and one sample label will be attached to the bag in which the filter material is placed.

D. Digital photographs will be taken of the sampler and filter train and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, start and end date and time, and collector initials.

F. After removing the dust sample, the used filter material will be placed in an appropriate collection bag or container, and the sample will be transported to an interim facility for packing and shipping.

G. Before shipping, dust filters will be re-weighed to the nearest gram. The information will be recorded in the appropriate field laboratory notebook.

H. All surfaces and instruments that might contact the dust samples will be rinsed with reagent grade acetone or hexane before and after filters are handled.

I. If a sufficient amount of dust is collected, a split dust sample will be retained for additional analysis if needed.

J. Dust filter samples will be placed in pre-labeled, chemically clean I-CHEM jars or other appropriate shipping containers, and will be immediately placed on ice and shipped to the laboratory. Duplicate or split samples will be similarly preserved and shipped.

4.6 Preservation of Sample Integrity

The primary quality assurance (QA) consideration in sample collection, processing, preservation, and shipping procedures is the preservation of sample integrity to ensure the accuracy of target analyte analyses. Sample integrity is

preserved by prevention of loss of contaminants already present in the personal dust sample and prevention of extraneous contamination.

All potential sources of contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. Ice chests will be scrubbed clean with detergent and rinsed with distilled water after each use to prevent contamination. To avoid contamination from melting ice, samples will be placed in waterproof plastic bags. Sampling equipment that has obviously been contaminated will be cleaned or not be used. All equipment that will be used directly in handling personal dust samples will be cleaned prior to each sampling trip, rinsed in acetone and pesticide-grade hexane, and stored in aluminum foil until used. Between samples, the field collection team will clean any preparation surfaces by rinsing them with acetone and hexane and mopping with bleach at the end of the sampling period or as necessary.

Ideally, all processing of collected dust after it is removed from the air sampler will be performed under clean room conditions to reduce the possibility of sample contamination. If additional sample preparation must be performed in the field, a clean area will be set up away from sources of contamination to help reduce the potential for inadvertent surface and airborne contamination of the samples. If sample processing is conducted in the field, a notation will be made in the field records and on the sample processing record.

4.7 Field Record-Keeping

Thorough documentation of all personal dust sample collection and processing activities is necessary for proper interpretation of personal dust sampling results. The data collection phase includes the completion of a various sample-tracking forms, which includes information regarding the sample collection procedures. The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel will be properly trained in these areas and perform these tasks in secured access facilities.

Field personnel will document all sampling activities in accordance with the Work Plan. During mobilization, pre-printed sample labels will be used. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted following the same labeling conventions.

Four separate preprinted sample tracking forms will be used for each sampling site to document field activities from the time the sample is collected through processing and preservation until the sample is delivered to the processing

laboratory. These are 1) Field record form; 2) Sample identification label; 3) Chain-of-custody (COC) label or tag; and 4) COC form.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection and (b) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

4.8.1 Field Record Form

For each individual personal dust sample that is collected, the following observations and measurements will be recorded at a minimum:

- Sampler number
- Start and end date and time collected
- Volume of air sampled
- Pre and post calibration information
- Temperature and weather conditions
- Site location and GPS coordinates
- Pre and post weight of filter
- Collectors name(s) and signatures
- Affiliation (including telephone number and address)

An example field record form is provided in Appendix A.

4.8.2 Sample Identification Label

During sampling preparation, sample labels will be pre-printed with the project name and a unique sample identification number. After sample processing and just prior to being secured to the sample container in the field, the following information will be added to the label in indelible ink for each individual specimen: (a) data and time of collection; (b) temperature and weather conditions; and (c) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number developed following the same format.

Personal dust samples shall be labeled with a unique number designated with a letter code for sample type followed by a six-digit designation of the day, month and year the sample was collected. This will be followed by the Study Area-

specific sample location number and a running number for that site. Sample types should be identified as follows:

PAS–Personal Air Sample

For example: **PAS031506-01-01** is the first personal air sample collected on March 15, 2006 from Farmer No. 1.

Quality Assurance/Quality Control samples should be designated in the same manner as above with no modification. Spikes and double spikes will be submitted to the laboratory as a blind. Sample type and numbers will be recorded on the field sample forms.

A completed sample identification label will be taped to each container and the individual filter sample will be placed in a waterproof plastic bag.

4.8.3 Chain-of-Custody Label

A COC label will be completed in indelible ink for each individual Dust sample. This would include the following information:

- Unique sample identification number
- Collector identification and signature
- Sampling start and end date/time
- Processing and analysis requested
- Preservation method (wet/dry ice)

After all information has been completed, the COC label will also be taped or attached with string to the outside of the waterproof plastic bag containing the individual sample. Information on the COC label will also be recorded on the COC form.

4.8.4 Chain-of-Custody Form

Personal dust samples collected for analysis will be tracked in the field and in transit to the processing laboratory and then to the analytical laboratory. Individual personal dust sample containers will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. A COC form will be completed in indelible ink for each shipping container (*e.g.*, ice chest) used. All pertinent information will be entered into the chain-of-custody form in the field including in-transit and laboratory delivery relinquishment or receipt information. Chain-of-custody forms include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection;

5) date and time of sample preparation for analysis; 6) date and time shipped/received; 7) sample designation; 8) signatures of individuals involved in sample transfer; 9) delivery address and method; and 10) the air bill or other shipping number, if applicable. The completed chain-of-custody form and a copy of the field record sheet will be signed, dated, enclosed in a sealable, waterproof plastic bag. This plastic bag will be taped to the inside cover of the ice chest so that it is maintained with the samples being tracked. Ice chests will be sealed with reinforced tape for shipment.

Field personnel will retain a copy of the chain-of-custody form and an additional copy will be transmitted to the project manager or the manager's designee. Samples will be considered in the sampler's custody while in sight, or locked in a secure area prior to shipment. All people involved in the handling and packing of the sample must sign the chain-of-custody form. Upon receipt at the processing or analytical laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples at each location shall check the actual samples against the chain-of-custody forms upon arrival. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained at the analytical laboratory.

4.8.5 Field Logbook

In addition to the four-sample tracking forms discussed above, the field collection team will document in a field logbook any additional information on sample collection activities, weather conditions, equipment operations, or any other unusual activities observed or problems encountered that would be useful in evaluating the quality of the dust sample data. This will also include method of sampling, air volume sampled, calibration data, start time, ending time, sampling duration, sampling location, and sampling conditions.

5.0 DATA QUALITY OBJECTIVES

Data Quality Objectives (DQOs) guide data collection and analysis to ensure that data are of adequate quality and sufficient quantity to support decision-making for evaluating human health concerns. DQOs are determined by the anticipated end uses of the data to be collected. In accordance with US EPA policy, DQOs should be developed for each data collection activity.

The DQOs for collection of dust samples are as follows:

- Determine the concentration of PCDD/Fs in the airborne dusts and compare these levels to human health benchmark concentrations, risk-based levels, or background levels as appropriate, based on project objectives.

- Obtain the necessary data to characterize the potential hazard to human health from exposure to these dusts.

All samples that are collected are to be used to provide data on Study Area characterization, human health and safety, and for use in the Human Health Risk Assessment (HHRA) to be performed.

5.1 Analytical Support Level

Analytical data generated under this Study Plan should be consistent with the data collection and risk assessment (USEPA analytical support Level III to V) when sampling contaminated media at human exposure points. Unless otherwise specified, laboratory analysis of all environmental and Quality Assurance/Quality Control (QA/QC) samples should be of Level IV. As specified in Level IV criteria, only approved USEPA analytical methods should be used corresponding to current Contract Laboratory Program (CLP) or SW-846 methodology.

5.2 PARCC

Data quality assessment parameters of precision, accuracy, representativeness, completeness, and comparability (PARCC) should be specified to establish acceptance criteria for all analytical data. These DQOs are expressed as quantitative and qualitative statements concerning the type of data needed to support a decision based on a specified level of uncertainty.

5.2.1 Precision

Precision is a measure of mutual agreement among replicate (or between duplicate) or co-located sample measurements of the same analyte. The closer the numerical values of the measurements are to each other, the more precise the measurement. Precision is determined by the spread of data about their mean. The spread presents how different the individual reported values are from the average reported value. Precision is thus a measure of the magnitude of errors, and should be expressed as the relative percent difference (RPD) between the analyte in a sample and associated duplicates.
This quantity is defined as follows:

$$RPD\ (\%) = 100 \times \frac{|S - D|}{(S + D)/2}$$

where: S = concentration of an analyte in a sample
D = concentration of an analyte in a duplicate sample

In addition, precision should be maintained by conducting routine instrument checks to demonstrate that operating characteristics are within predetermined limits.

5.2.2 Accuracy

Accuracy is a measure of bias in a measurement system. The closer the value of the measurement agrees with the true value, the more accurate the measurement. This should be expressed as the percent recovery of an analyte from a surrogate, matrix spike, or standard reference sample. These samples, having known analyte concentrations, should be analyzed in the laboratory for comparison.

Accuracy measures the average or systematic error of an analytical method. This measure is defined as the difference between the average of reported values and the actual value. Accuracy should be expressed as the percent bias. The closer the value is to zero, the more accurate the data. This quantity is defined as follows:

$$Bias\ (\%) = \frac{MC - KC}{KC} \times 100$$

where: KC = known concentration of an analyte
MC = measured concentration of an analyte

5.2.3 Representativeness

Representativeness is a qualitative parameter that expresses the degree to which sample data accurately and precisely represents a characteristic of a population, parameter variations at a point, or an environmental condition. The design and rationale for the sampling program previously described ensures that the environmental conditions present in the Study Area should be sufficiently represented.

5.2.4 Completeness

Completeness is a measure of the number of valid measurements obtained in relation to the total number of measurements planned. The closer the numbers are the more complete the measurement process. Completeness should be expressed as the percentage of valid to planned measurements and is calculated as follows:

$$\text{Completeness (\%)} = \frac{V}{P} \times 100$$

where: V = number of valid measurements
P = number of planned measurements

5.2.5 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared to another. Data sets should be compared only when precision and accuracy meet the specified acceptance criteria. Sample data should be collected and reported in order to be comparable with other measurement data for similar samples. Comparability should be maintained through consistency in sampling conditions, selection of sampling procedures, analytical methods, and data reporting units. The US EPA CLP or SW-846 analytical methods selected for this investigation should be commensurate with those from previous investigations at the Study Area to assure comparability with other data sets.

5.3 Quality Control Checks

Quality control checks of both field sampling and laboratory sample analysis should be used to assess and document data quality. The collection and analysis of the quality control samples described below should be used for this purpose. Results from these quality control samples should be employed to determine the precision of sample collection and handling procedures, the accuracy of the

laboratory analysis, the thoroughness of field equipment decontamination procedures, and the representativeness of the environmental samples.

5.3.1 Field Duplicates/Replicates

Field duplicates (or replicates) may be collected at selected locations to evaluate the environmental variability at a location and the precision of laboratory measurement if it is determined that such a need and sufficient sample quantity exists. Field duplicates can be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping although field blanks may suffice in this complicated sampling. If needed, field duplicate samples should be provided to meet US EPA's recommendation that such samples should be submitted at a rate of five to ten percent of the total number of samples.

5.3.2 Field Blanks

Field blanks should be used to indicate the presence of external contaminants that may have been introduced into the samples during the collection, transport and analytical processes. Field blanks will be prepared in the Study Area during the sampling event. A field blank will consist of clean, unused filter material that is prepared, stored, and analyzed for PCDD/PCDF congeners as if it were an actual sample. These samples will be handled in the same manner as those used in the actual sampling of the Study Area. At least one field blank will be analyzed for each sampling event.

5.3.3 Matrix Spike/Matrix Spike Duplicates

In addition to the control samples identified below, the laboratory should use a series of control samples as specified by the CLP or SW-846 method. These include a method blank, surrogate, matrix spike, and matrix spike duplicate. Two additional personal dust samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. Matrix spike/matrix spike duplicates (MS/MSD) should be prepared and analyzed for selected samples at a minimum of five percent of the total number of environmental samples collected for each matrix. The matrix spikes for dust samples will consist of personal dust from samples collected spiked with known concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. Analysis of these duplicate samples should be performed for samples of similar matrix type and concentration, and for each sample batch (sample delivery group) of no more than 20 samples. Quality control samples should be handled and analyzed in the same manner as all environmental samples.

In general, MS/MSD samples will be prepared by the laboratory, identification and the concentrations will be based on the estimated concentration of contaminants, and the characteristics of each matrix. Field personnel will introduce spikes as blind samples for analysis.

5.3.4 Reporting Limits

Data quality needs are met by the CLP contract required detection limits (CRQLs), or the SW-846 method detection limit for each analyte. At a minimum, detection limits must be below the potential safe human levels applied to the data. The detection limits of the analytical procedures need to be sufficiently low to allow reliable quantitation of the target analytes in personal dust samples from farmers working agricultural soils at various locations along the Tittabawassee River floodplain. In the case of congener-specific PCDD/Fs analyses, the detection limit selected is generally in the range of 0.1 part per trillion (ppt) in view of the likely amount of dust available for analysis. Non-detects will be handled as Limit of Detection (LOD) = 0.

The detection limits specified in the US EPA analytical methods for this study satisfy the DQOs for this investigation. The use of standard sampling methods, US EPA analytical methods, and data validation ensures that detection limits will be useful for conducting assessments of public health, and comparable to previous dust studies.

5.3.5 Data Validation

Once results of the laboratory analyses have been completed, the average concentrations of PCDD/F detected in personal dust samples across sampling locations will be calculated. The data evaluation will review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet that includes sampling ID number, sampling location, start and end date and time of sample collection, sample type, and PCDD/F concentrations in the dust. The data entry will be verified to ensure the accuracy of the information.

- All decisions and recommendations should be based upon validated analytical data. All analytical data generated by the laboratory should be validated in accordance with the quality control criteria specified in the US EPA CLP statements of work. The purpose of the validation process is to eliminate unacceptable analytical data, and to designate a data qualifier for any data quality limitation discovered. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination. An assessment of data usability should

determine the degree to which validated data are suitable for the purposes intended, and whether the data are useful for other purposes.

5.3.5.1 Detection Limit Issues for Dust Sampling

The US EPA Contract Laboratory Program (CLP) for dioxins and furans (http://www.epa.gov/superfund/programs/clp/dlm2.htm) indicates a quantitation limit of 1 pg/g TCDD/F up to 10 pg/g OCDD/F for a sample size of 10 grams of soil. The limit is apparently driven mostly by interferences. This suggests a practical problem with the personal dust sampling that may not be resolvable

For personal air sampling, dust samples that weigh only in the tens of milligrams for individual samples at most will likely be collected. For instance, the study would get 30 mg of dust only if the air concentration of suspended dust is 10 mg/m^3 average and three days of samples were composited. This seems potentially unlikely. More likely is <1 mg/m^3 average, implying sample sizes of only 3 mg or less. In this case, the study will result in mostly non-detects for all analytes.

If only 30 mg are collected, this suggests quantitation limits no better than 300 pg/g TCDD/F to 3000 pg/g OCDD/F. For 2,3,4,7,8-PeCDF that dominates in the soil along the river, the detection limit is 5 pg/g for 10-gram sample size, indicating around 1500 pg/g for a 30 mg sample. The median soil concentration (N= 30) for 2,3,4,7,8-PeCDF is 800 ng/kg, so we would expect to get mostly non-detects unless sample size can be increased or detection limits decreased. Similarly, for 2,3,7,8-TCDF, the detection limit is 1 pg/g for a 10 grams sample, suggesting around 300 pg/g for a 30 mg sample size. Median soil concentration along the river (n= 30) is 2000 pg/g, so it is possible a reasonable detection rate might be achieved in this case.

However, the resultant TEQ calculations would get badly skewed if this issue cannot be satisfactorily resolved since the major contributor to TEQ along the river is 2,3,4,7,8-PeCDF. These detection limit issues might possibly be improved somewhat by more samples and larger composites or special handling in the laboratory, but this needs to be resolved before attempting this study.

5.3.6 Data Analysis

The objective of data analysis is to identify and report the PCDD/F concentrations measured in personal dust samples that have been collected from the study area, calculate summary statistics (*i.e.*, range, mean, 95% confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error.), and develop a valid PDF for use in exposure and risk assessment. These steps will be outlined in the Exposure Assessment Work Plan. Ultimately, this information will be used to calculate the potential risk of PCDD/F exposure to humans.

6.0 DATA COLLECTION METHODOLOGY

6.1 Personal Air Monitoring Sampling

Study Area personnel will keep a log of sampling activities on the Field Sample Form (Appendix A). Information included on the field sample form will consist of pre and post calibration information, weather and other environmental parameters, farmer and sample numbers or designation, location, time in Study Area, personnel and equipment present, down time, materials used, any equipment failures or protocol changes, and any other pertinent information necessary to reconstruct field activities at a later date.

6.1.1 Personal Air Monitoring Sampling Procedures and Equipment

All personal air-sampling pumps will be calibrated prior to and after use at the Study Area and all batteries adequately charged to allow for a full, eight-hour (or longer) sampling period. The pumps shall be calibrated for approximately 2 L/min rate and only clean tubing and filter holders are to be used at the Study Area. Filter cassettes or trains will be prepared prior to entering the field and sealed until ready for use. On arrival at the Study Area, sampling personnel shall place all air sampling pumps on the test subject such that the pump is on the belt or waistband and the filter train is attached to the collar. The collection orifice should face downward and be free of any obvious obstructions to air flow. All pumps will be turned on at the beginning of the work shift and, throughout the sampling period, sampling personnel shall inspect the pumps to ensure that they are operating correctly and that no filter clogging has occurred. If a pump needs to be switched or filters changed out, this information will be noted in the field records

At the end of the sampling period, the filter apparatus shall be sealed. Volume of air sampled and time sampled will be recorded for each individual sample, even those that may be composited later. Post calibration shall be conducted using the field sample. All final samples will be placed in secondary, labeled, and separate containers to protect the sample during transport to the analytical laboratory.

All sampling, calibration, data collection, and documentation will be conducted under supervision.

6.2 Sample Containers and Handling

After sample processing, each filter sample, blank or duplicate will be individually stored in chemically clean glass containers. The sample identification label will

be taped to the outside of each container, each container will be placed into a waterproof plastic bag and sealed, and the COC tag or label attached to the outside of the plastic bag with string or tape. All of the packaged individual samples from the same locations will be kept together (if possible) in one large waterproof plastic bag in the same shipping container (ice chest) for transport for further preparation. Once packaged, samples will be cooled on ice immediately.

Sample transport containers should be affixed with a sample label that should be filled out at the time of collection. Information on the sample label should include, at a minimum, the following: (1) Study Area location, (2) sample numbers, (3) date and time of sample, (4) initials of sampler, and (5) parameters to be analyzed. Chain-of-custody forms will be initiated at the time of collection by the sampler.

6.3 Sample Preservation

The type of ice to be used for shipping will be determined by the length of time the samples will be in transit to the processing laboratory and the sample type to be analyzed. Wet ice or blue ice (sealed pre-frozen ice packets) is recommended as the preservative of choice if the samples will be delivered to the processing laboratory within 24 hours. If the shipping time to the processing laboratory exceeds 24 hours, dry ice will be used.

A secure freezer unit may be used for temporary storage of personal dust samples. Long-term storage of remaining samples (until study termination) will take place at an off-site storage location yet to be determined. Personal dust filter samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University, or an equivalent facility, where they will be stored at –20°C until shipped. All samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified above.

6.4 Sample Shipping to Laboratory

The personal dust samples will be hand-delivered or shipped to the analytical laboratory as soon as possible after collection and initial processing following US EPA/REAC guidelines (US EPA, 1994).

Shipping materials needed may include:

- Inert packing material
- Sample containers

- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape
- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)

Personal dust filter samples will be transported to the laboratory within 48 hours for processing. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Field collection staff will ensure the samples are packed properly with adequate ice layered between samples so that sample degradation does not occur. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there may be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked.

Sufficient wet or dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours, if necessary. To allow ventilation of the dry ice, coolers with airtight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures. In addition, a member of the field collection staff will telephone ahead to the processing location to alert them to the anticipated delivery time of the samples and the name and address of the carrier to be used (if shipped). Field collection staff will avoid shipping samples for weekend delivery to the processing location unless prior plans for such a delivery have been agreed upon with the processing staff. The time the samples were collected and time of their arrival at the processing facility will be recorded on the COC form.

7.0 DECONTAMINATION/INVESTIGATION-DERIVED WASTES

Applicable decontamination and waste handling procedures are addressed in this section.

7.1 Decontamination

Due to the nature of the material to be sampled, a centralized decontamination area is not deemed necessary for this Study Area. Appropriate cleansing of preparation areas to prevent cross contamination has been previously discussed.

7.2 Investigation - Derived Waste Collection and Storage

Anticipated solid wastes from this sampling activity include latex gloves and sample labeling materials. A designated waste bag will be established for stockpiling and storage of these materials. Study Area personnel will be responsible for final disposal of the waste.

8.0 REFERENCES

American Society For Testing And Materials, Standard Test Method for Particle Size Analysis of Soils, Designation D 422-63, Reprinted from the Annual Book of ASTM Standards, Philadelphia, PA.

Environmental Protection Agency and Michigan State University. (2005). Dioxin contamination and the Tittabawassee River and Floodplain. Managing the risks: An issue guide.
http://www.nifi.org/stream_document.aspx?rID=3926&catID=15&itemID=3925&typeID=8

Saginaw County Chamber of Commerce. (2006). Relocation information. Website visited on 3/21/06. http://www.saginawchamber.org/Chamber/facts1.htm

U.S. Census Bureau. (2001). Census 2000: Table DP-1. Profile of General Demographic Characteristics. Geographic area: Saginaw County, Michigan.
http://censtats.census.gov/data/MI/0602614579840.pdf

US Department of Agriculture. (2003). 2002 Census of Agriculture county profile: Saginaw, Michigan.
http://www.nass.usda.gov/census/census02/profiles/mi/cp26145.PDF

US Environmental Protection Agency. (2006). Saginaw River/Bay Area of Concern. Website visited on 3/21/06. http://www.epa.gov/glnpo/aoc/sagrivr.html

Appendix A - Sampling Form

LOCATION: _____ **DATE:** _____ **Pg.** _____ **of** _____

ADDRESS: _____ **SITE REF. #:** _____

_____

AREA/WORKPLACE: _____

WORKER: _____ **SAMPLER:** _____

ID #: _____ **SHIFT:** _____ **BARAMETRIC PRESSURE:** _____

JOB TITLE: _____ **TEMP:** _____ **HUMIDITY:** _____

_____ **WIND SPEED:** _____ **DIRECTION:** _____

NOTES ON : TIME / TASK DESCRIPTION / EQUIPMENT AND PPE

PUMP S/N: _____

SAMPLE DATA	SAMPLE #:	SAMPLE #:	SAMPLE #:	SAMPLE #:
START TIME				
STOP TIME				
TOTAL TIME				
TYPE				
STRATEGY				
SUBSTANCE(S)				

PRE-CALIBRATION: **LOCATION:**_____

PUMP MFG:_____ **S/N:**_____

CAL. METHOD:_____ **DATE:**_____

CAL. BY:_____ **FLOW RATE:**_____

POST-CALIBRATION: **LOCATION:**_____

DATE:_____ **CAL. BY:**_____

FLOW RATE:_____ **AVE. FLOW RATE:**_____

CALCULATIONS

SAMPLE RESULTS **LAB. USED:**

SAMPLE #	SUBSTANCE(S) / SAMPLE METHOD(S)	TOTAL TIME	FLOW RATE	VOLUME	AIR. CONC	TWA $_8$	OEL

ATTACHMENT G

TECHNICAL MEMORANDUM

COMPARISON OF DIOXIN ANALYTICAL RESULTS (ROUND ROBIN)

Objective

The Dow Chemical Company has conducted two series of Round Robins. The first round robin analyzed samples taken by Michigan State University for the Tittabawassee River Wild Game Study. The second round robin analyzed samples taken from samples along the Tittabawassee River floodplain. The objective is to identify laboratories with the capabilities of meeting the following requirements:

1. The laboratory employs staff that is experienced in High Resolution Mass Spectrometry methodology, can successfully analyze samples and overcome technical issues that require in-depth problem solving beyond normal production style operations. All of these tasks must be conducted while maintaining schedules and data quality within the confines of a commercial production environment.
2. The laboratory has developed a standard data presentation format that can routinely produce a data package with good documentation of all associated sample issues and demonstrate completeness of all required QA/QC procedures. Additionally, the report must convey to the reader all observations and experiences during the time of preparation and analysis that influenced the quantitation. The data package should be presented in a clear and logical order that provides complete documentation of all pertinent information, demonstrate traceability at all stages of analysis and demonstrate a sound scientific approach.

All laboratories involved in this event demonstrated the technical capabilities to report hardcopy data within the required turnaround times. Some laboratories experienced difficulties in reporting the EDD which required a higher level of effort from both sides of the project to execute this task. None of the commercial laboratories reported data that would be rejected, but the data quality did vary from one company to the next.

Scope and Results

Tittabawassee Floodplain Samples

In preparation for the Remedial Investigation and Midland Bioavailability studies, a Round Robin study that included six laboratories throughout the United States, Belgium, Germany and Canada was conducted from November 2005 - April 2006. The objective of

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this study was to select an alternative laboratory to analyze dioxin/furans in soils and sediment samples taken from the Tittabawassee River and Floodplain and the City of Midland under approved work plans.
Soil samples were taken from Tittabawassee Floodplain located in an area previously identified in the Tittabawassee Floodplain Scoping Study as Area 1. Located just south of Gordonville Road and N Saginaw Rd, Area 1 was selected to offer a relative comparison of results expected from the Round Robin. A total of nine samples were taken from Area 1 and sent to the following labs for analysis according to EPA Method 1613B:

- Alta Analytical, Inc. (El Dorado Hills, CA)
- AXYS (Sidney, British Columbia, Canada)
- GfA (Hamburg, Germany)
- The Dow Chemical Company Trace Analysis Group (Midland, MI)
- Paradigm (Wilmington, NC)
- SGS (Antwerpen, Belgium)

Tittabawassee Floodplain Sample Results

A final report of the laboratory round robin results will be made available once the completed package is received and validated (Level IV) from GfA. We anticipate this should be finalized by July 15, 2006.

Wild Game Study Samples

Biological samples from wild game collected by Michigan State University were homogenized, split, coded and sent to the following labs for analysis:

- Alta Analytical, Inc. (El Dorado Hills, CA)
- AgriQuality (Wellington, New Zealand)
- The Dow Chemical Company Trace Analysis Group (Midland, MI)

Wild Game Study Sample Results

Both Alta and AgriQuality conducted their analyses according to EPA Method 8290A. The Dow Trace Analysis Group used EPA Method 1613B. Comparison of the data between Alta Analytical and AgriQuality indicated that both datasets are comparable and of acceptable quality.

Data Validation

Level III and IV data validation was performed for both Wild Game and Tittabawassee Floodplain Sample results, with the exception of GfA. Dow is still awaiting a completed

data package from GfA. Validated data for the Floodplain Samples results were submitted to the MDEQ in the Environmental Monitoring Report, 1st Quarter 2006. Validated data from GfA will be submitted in the Environmental Monitoring Report, 2nd Quarter, if available.

Lab Audits

In order to certify that analytical laboratories selected to perform analysis for Dow operates according to Dow's own QA/QC criteria, an independent consultant conducts in-person multi-day visits to the analytical laboratory to interview staff, verify procedures, methods and training. The results of these laboratory audits are communicated back to Dow. Follow-up communication with the laboratory is established to affirm the results and follow-up on any suggestions for changes identified by the audit, if any.

ATTACHMENT H
Soil/Dust/Sediment Exposure Data Quality Objectives

Study Objectives

1. To describe how soil and sediment will be collected for the nature and extent portion of the Remedial Investigation and be used to provide the necessary data for use in the Human Health Risk Assessment (HHRA).

2. To identify the vertical and horizontal soil or sediment samples that will be used to estimate human exposure in the various land uses and relevant exposure pathways.

3. To identify other sources of useful information on target analyte residues in soil and dust (*i.e.*, the University of Michigan Dioxin Exposure Study - UMDES) that can be combined with RI data to better characterize potential exposure

1.0 Introduction

Soils along the Tittabawassee River and within City of Midland study areas are known to contain polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and may also contain other target analytes (TAs) that have not yet been determined. In some areas soil concentrations of PCDD/Fs are greater than Part 201 generic cleanup criteria, and these affected soils correspond to various land uses. Human activities vary according to land use and will dictate the manner and extent of exposure to TAs in soil. Under Part 201 and in accordance with standard HHRA practices (US EPA 1991; 1995; 1996; 2002), soil exposure pathways will be identified and evaluated for each relevant land use category. To represent the varying nature of soil exposures, it is important that soil (or sediment) samples be collected from appropriate locations and depths to provide usable data for the HHRA.

This Study Plan supplements the soil sampling plans and describes how the soil data will be collected, evaluated (including the evaluation of existing data), and arrayed to properly assess human risk from exposure to Study Area soils. The sampling and analysis plans (SAPs) developed for the RI will present the sampling design with specified sampling locations, field methods, equipment and analytical methods, and will be developed with input from the HHRA team to ensure the samples are useful for the HHRA. The specific SAPs will address the data quality objectives (DQOs) of identifying other TAs, defining nature and extent of site-related TAs, and characterizing fate and transport mechanisms are provided in the 2005 Remedial Investigation (RI) WPs for the two study areas, and will be supplemented by the 2006 RI SAPs.

It is important to ensure that the collection of RI samples will provide data that is usable for HHRA purposes. Consequently, limited HHRA DQOs are provided herein to augment the DQOs identified for the proposed RI sampling activities planned for the two study areas. The HHRA DQOs will also guide selection and incorporation of soil, sediment, or dust data from existing soil data (*e.g.*, prior scoping studies), the UMDES data sets, or soil or sediment data from the Michigan Department of Environmental Quality (MDEQ) or US EPA that may prove valuable as supplemental or validating data. Such data will first provide EPCs for each land use/exposure pathway and will ultimately be used/evaluated as the basis for the risk estimates in the context of each exposure scenario (*e.g.*, relevant exposure pathways, receptors, and land use categories) so that the type of data selected from previous and ongoing investigations accurately represents the TA concentrations that humans may actually be exposed to in soil/sediment or dust under certain conditions.

2.0 Conceptual Human Exposure Models

To guide the RI collection of soil samples for use in the HHRAs, several conceptual human exposure models (CHEMs), which are slightly revised from the February 23, 2006 submittal, were developed for each applicable land use category. While this discussion is limited to soils, the same considerations apply to dust or sediment exposures. The land use categories of relevance for both study areas are residential, agricultural, commercial, industrial, and recreational. The CHEMs identify the exposure pathways for human receptors present at each of the land use categories. The revised CHEMs are provided in Figures 1 through 3 for the Midland Study Area and Figures 4 through 6 for the Tittabawassee River Study Area.

As shown in the CHEMs, soil samples may ultimately need to be collected to represent TA exposure concentrations representing exposure pathways that have primary release mechanisms including:

1. Dust emissions
2. Direct soil contact
3. Root uptake
4. Animal uptake
5. Erosion

However, the approach to be taken in the HHRA renders some of these moot, by using measurements at different points along the exposure pathways. Thus evaluation of exposure point concentrations for animal uptake is rendered unnecessary (in the HHRA) by the planned, direct measurement of exposure point concentrations in animal products that are consumed. As additional soil, dust, or sediment data become available from the RIs or other data sources, the CHEMs may be modified and data collection and evaluation approaches adjusted accordingly to ensure that appropriate data continue to be obtained for the HHRAs.

3.0 Sampling Location Considerations

A determination of whether the proposed RI sampling locations are sufficient to adequately represent the spatial variability in soil TA exposure concentrations will not be known in detail until the RIWP soil sampling activities for the study areas are finalized and approved by the MDEQ. While it is plausible that the overall large-scale variability is adequately represented by existing sampling data, smaller scale variability necessary to evaluate land use/property-specific exposure units is not yet known for certain. This may be important for the HHRA and will be considered.

The applicability and effectiveness of a geospatial or geomorphological model to predict TA concentrations in unsampled areas will also be considered for developing land use-specific soil exposure concentrations estimates subject to regulatory approval. The sampling locations associated with prior soil sampling investigations and the UMDES sampling locations (if known), will be evaluated to determine if it is similarly representative of soil concentrations for the relevant pathways and land use categories, and if this data can be used to represent or supplement exposure associated with the various land uses or exposure pathways. The soil sampling data and locations represented by the various identified soil or sediment data sources will be collectively evaluated to determine if an adequate number of sampling locations have been sampled to construct representative exposure data sets for use in the HHRAs.

4.0 Sampling Depth Considerations

The primary release mechanism for the putatively major soil exposure pathways is direct contact and most of the release mechanisms similarly act at the soil surface. To assess current exposures, TA concentrations in the top inch are most representative. However, since such exposure need to be integrated over multiple years, and there are various processes that mix the soil, expose deeper layers, or cover current surfaces (*e.g.*, rainfall splash; bioturbation by soil animals; erosion and runoff), sampling over a greater vertical soil horizon may be more appropriate. Certain other human activities, such as gardening, landscaping, and field tilling are likely to result in exposure of and to deeper soils, but are expected to occur less frequently. Information obtained from implementation of a soil exposure behavioral-activity survey will help determine appropriate exposure frequency ranges to use in the HHRAs.

In erosional or depositional areas of the Tittabawassee River Study Area, the sampling depth interval will be matched, if possible, with erosion or deposition rates, to allow reasonable estimates of averages TA soil concentrations. Deeper contamination presumably only occurs in depositional areas, where the contamination would not be brought back up to the surface absent a change in conditions. Evaluation of the risk associated with soils deeper than six inches in the Study Area will be dependent upon the outcome of the geomorphic features and sampling to be conducted. In the event that an overall state of accretion can be documented along the river, the level of effort to evaluate subsurface soils (*i.e.*, deeper than six inches) may potentially be reduced.

Evaluation of the initial soil sampling showed that the distribution of concentrations in 0–1 inch, 1–3 inch, and 3–6 inch samples are statistically indistinguishable. Comparison of paired 0–1/1–3, and separately of paired 0–3/3–6 inch depth range samples (*i.e.* samples collected from different depth ranges at the same location) demonstrated no statistically significant differences between different depths, and the within-location (*i.e.* depth) variability was considerably smaller than the between-location (*i.e.* horizontal spatial) variability. Selection of particular depth ranges thus may be largely immaterial for HHRA purposes.

For Midland Soils Study Area, TAs are expected to have initially been present predominantly in near surface soils as a result of atmospheric deposition; but the deposition was sufficiently long ago that their current vertical distribution cannot now be predicted. MDEQ (2002) sampling strategies guidance for soil direct contact (*i.e.*, statistical guidesheet 19) recommends that if affected soils are "located at the immediate surface (such as through air deposition of hazardous substances), surface soil samples should represent the immediate surface (*e.g.*, top one inch)." However, soil samples will also be collected in selected areas from 1 to 6 inches to represent soil exposures that occur less frequently during gardening and landscape activities that would mix the soil.

5.0 Exposure Unit Considerations

Defining exposure units (EUs) is necessary to ensure that sampled areas will adequately represent the soil area over which exposures will occur, which is largely a function of human activity patterns summarized by a land use category. EUs may represent the area over which the receptor is expected to move randomly over time, such that equivalent amounts of time are spent at each location within the EU (MDEQ, 2002; EPA, 1996). Defining the EUs for the land use categories is also important for guiding selection of soil sample location data for calculation of EPCs to ensure that (horizontal) spatial variability in concentrations on the relevant scale can be estimated.

It is expected that the geospatial or geomorphological model will satisfactorily estimate concentrations of TAs, and their variability at relevant scales, throughout the Study Areas. Consequently, actual soil samples may not be collected within each distinct area that might be considered an EU, though some sample locations may exist within a particular land use EU. For HHRA purposes, the geospatial or geomorphological model needs to be sufficiently robust to estimate TA concentration distributions throughout the Study Areas at the spatial resolution required to represent exposures within the EUs for the land use categories.

If the degree of uncertainty of TA concentrations is considered too high for risk management purposes (the measurable components of this uncertainty will be incorporated in the risk assessment, so will be reflected in the risk estimates; but there are possibly unmeasurable components also), additional sampling may be needed to refine the model and support risk management decisions.

For the Midland Study Area, an evaluation of soil sampling locations associated with historic, UMDES, and proposed Phase I and II RI soil sampling locations will be collectively completed to determine if these sampling locations adequately represent land uses and their corresponding EUs. Overlaying property boundaries on the proposed sampling locations is necessary to complete this evaluation. The sampling locations may need to be adjusted to ensure that an appropriate number of samples are collected to adequately represent the determined EUs.

6.0 Data Quality Objectives

The DQO process is a planning tool used to avoid collecting data that are inconsequential to decision-making, and to ensure that data of sufficient quantity and quality are collected in accordance with the decisions needing to be made – i.e., that data are representative, reliable and specific to the decision. DQOs minimize expenditures related to data collection by eliminating unnecessary, duplicative, or unnecessarily precise data. The overall goal of the DQO process is to identify the type, quality, and quantity of data necessary to develop remedial response activities that are based on the results of HHRAs and its associated uncertainties.

DQOs are routinely developed during the planning stages of any exposure data collection effort, before the data are collected. The DQO process is also intended for use after data collection, to guide use of data in the decision process as well as the collection of additional data which may be needed to fill data gaps specific to the decision. Essentially, the DQO process is interactive and may undergo changes as more information becomes available (DOE, 1994). In exactly this vein, the data used in the HHRA may consist of a mixture derived from currently available data, Phase I and II RI data, or UMDES data. Moreover, Phase II data collection will largely fill data gaps identified by the HHRA, based on risk management requirements.

The U.S. Environmental Protection Agency (USEPA) guidance document, *Guidance for the Data Quality Objectives Process* (USEPA, 2000) outlines a seven-step process for establishing DQOs. These steps are listed below; however, some are not relevant to the HHRA DQOs.

- **State the problem.** Concisely describe the problem to be solved: background information and what information is missing.

- **Identify the decision.** Identify the decision that must be made to resolve the problem.

- **Identify the inputs to the decision.** Identify the information or data needed to make the decision.

- **Define the study boundaries.** Specify the conditions (time periods, spatial areas, and situations) to which the decision will apply and within which the data will be collected.

- **Develop a decision rule.** Define the conditions by which the decision maker will choose among alternative risk management actions. This is usually specified in the form of an "if. . . then . . ." statement.

- **Specify acceptable limits on decision errors.** Define the decision maker's acceptable uncertainty based on the consequence of making an incorrect decision.

- **Optimize the sampling design.** Evaluate the results of the previous steps and develop the most resource-efficient design for data collection that meets all of the DQOs.

7.0 HHRA Data Quality Objectives

The DQO problem statements that correspond with the HHRA data needs for the Midland and TRFP Soils study areas are:

- **DQO 1:** Guide RI soil sample collection processes to obtain data representative of soil exposure, allowing estimates of human health risk.

DQO 1: Generate representative soil exposure data sets

The DQO process outcome for the DQO 1 problem statement for the TRFP Soil and Midland Soils study areas are summarized below in Table A.1 and A.2, respectively. DQOs related to additional HHRA sampling objectives that may arise during the course of the RI will be developed after RI WP sampling, analysis, and data evaluations are completed and as the RI progresses.

Table A.1. Tittabawassee River Soils Study Area
DQO 1: Obtain representative soil exposure data sets for the HHRAs

Problem Statement	Soil sample data should represent the TA concentrations that humans will be exposed to in soil. Although initial RI phase soil data collection is designed for other purposes (TA identification, nature and extent and fate and transport) information can be obtained at the proposed locations to provide soil exposure data for HHRA purposes. This will ensure collection of the type of data necessary to generate appropriate data sets to estimate human health risk. The subsequent evaluation of these data sets in the HHRAs will facilitate the development of appropriate response activities.
Decision to be Made	Are the soil TA exposure concentrations representative of the exposure pathways for each land use category?
Inputs to the Decision	• Land use. • Sample location. • Behavioral-activity survey WP to determine activity types and the depth of soil contact during these activities • Soil depth interval representative of ingestion, dermal and inhalation exposure pathways for the land use category.

Table A.1. Tittabawassee River Soils Study Area
DQO 1: Obtain representative soil exposure data sets for the HHRAs

Study Boundaries	• Longitudinal boundary: Midland Plant to the confluence with the Saginaw River (excluding areas around the Midland Plant) •
Decision Rules	• If soil samples collected are sufficient and reliably represent land use category exposures then average exposure point concentrations for appropriate exposure unit sizes can be calculated to evaluate exposure that may occur on a daily basis. Daily exposure to soils through the identified exposure pathways is likely for residential and agricultural land uses. Exposure to soils for commercial, industrial and recreational land uses is expected to occur less frequently
Acceptable Limits on Decision Errors	Enough samples should be collected to support calculation of reliable and representative estimates of the TA soil concentrations that humans will be exposed to for each pathway and land use category. Existing and Phase I sample results will be evaluated to develop the preliminary geospatial model. If the degree of uncertainty in geospatial model estimates of furan and dioxin concentrations is too high for risk assessment or remedial planning purposes, then additional sampling will be conducted during Phase II of the RI to refine or replace the model.
Optimized Sampling Design	Additional soil sample collection during Phase II may be necessary to validate predictions of the geospatial model to assure that exposure unit TA concentrations are reliable and representative measures of exposure for the relevant pathways and land uses.

8.0 Conclusion

The HHRA team will work with MDEQ to resolve any issues identified in this Study Plan to assure that representative data sets are developed to estimate health risk, or compare to appropriate soil criteria for the identified relevant land use categories and human exposure pathways.

9.0 References

MDEQ (Michigan Department of Environmental Quality). 2002. Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria. Environmental response Division.

US DOE (U.S. Department of Energy). 1994. Using the Data Quality Objectives Process in Risk Assessments. Office of Environmental Guidance. CERCLA Information Brief. EH-231-023/0794.

US EPA (U.S. Environmental Protection Agency). 1991. Risk Assessment Guidance for Superfund: Volume I – Human Health Evaluation (Part B, Development of Risk-based Preliminary Remediation Goals). Office of Research and Development. EPA/540/R-92/003. December 1991.

US EPA (U.S. Environmental Protection Agency). 1995. Land Use in the CERCLA Remedy Selection Process. Office of Solid Waste and Emergency Response. OSWER Directive No. 9355.7-04. May 25, 1995 Memorandum.

US EPA (U.S. Environmental Protection Agency). 1996. Soil Screening Guidance: Technical Background Document. Office of Solid Waste and Emergency Response. EPA/540/R95/128. May 1996.

US EPA (U.S. Environmental Protection Agency). 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites. Office of Solid Waste and Emergency Response. OSWER Directive No. 9355.4-24. December 2002.

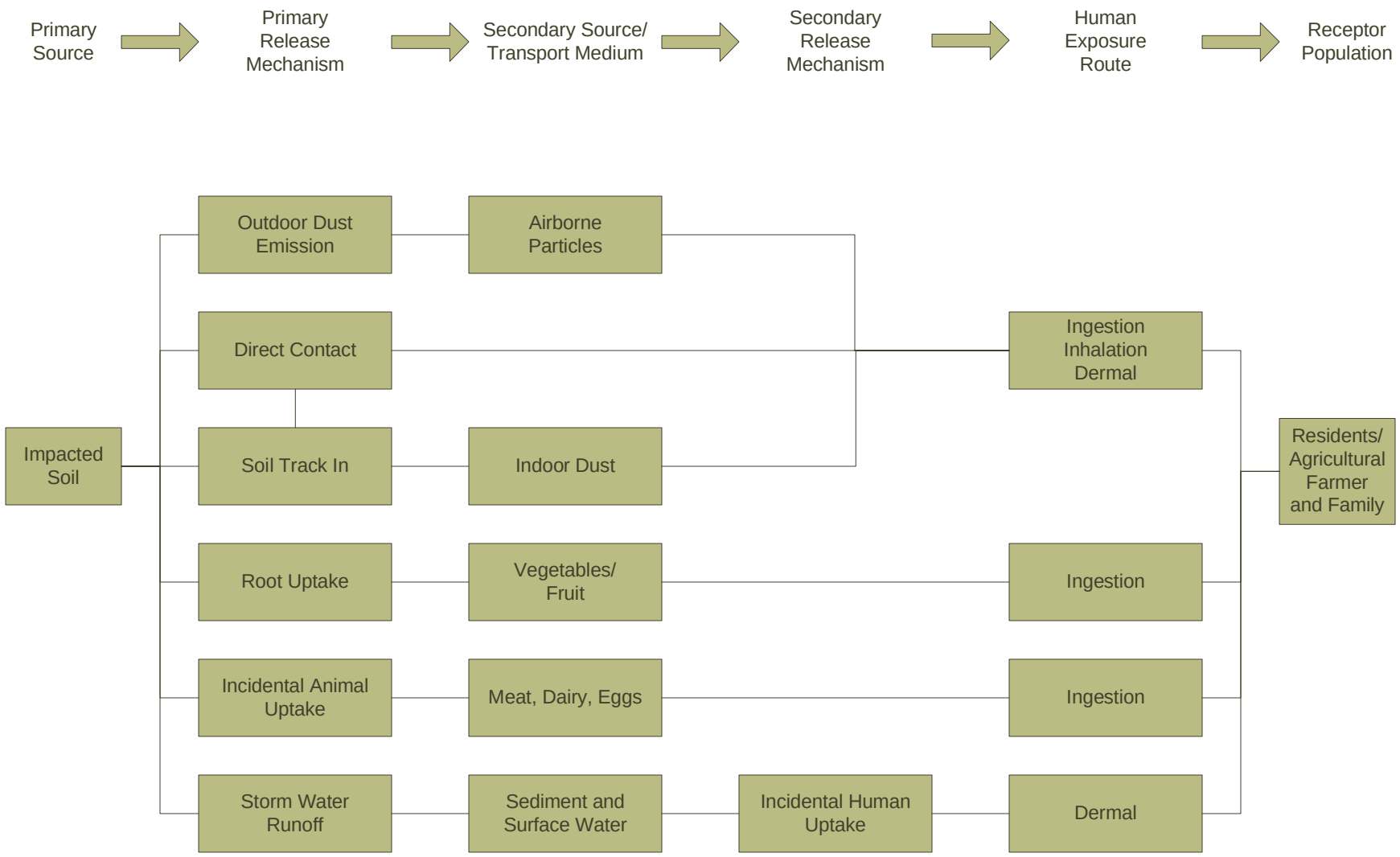

Figure 1. Midland Area Soils Conceptual Human Exposure Model for Residential and Agricultural Land Uses

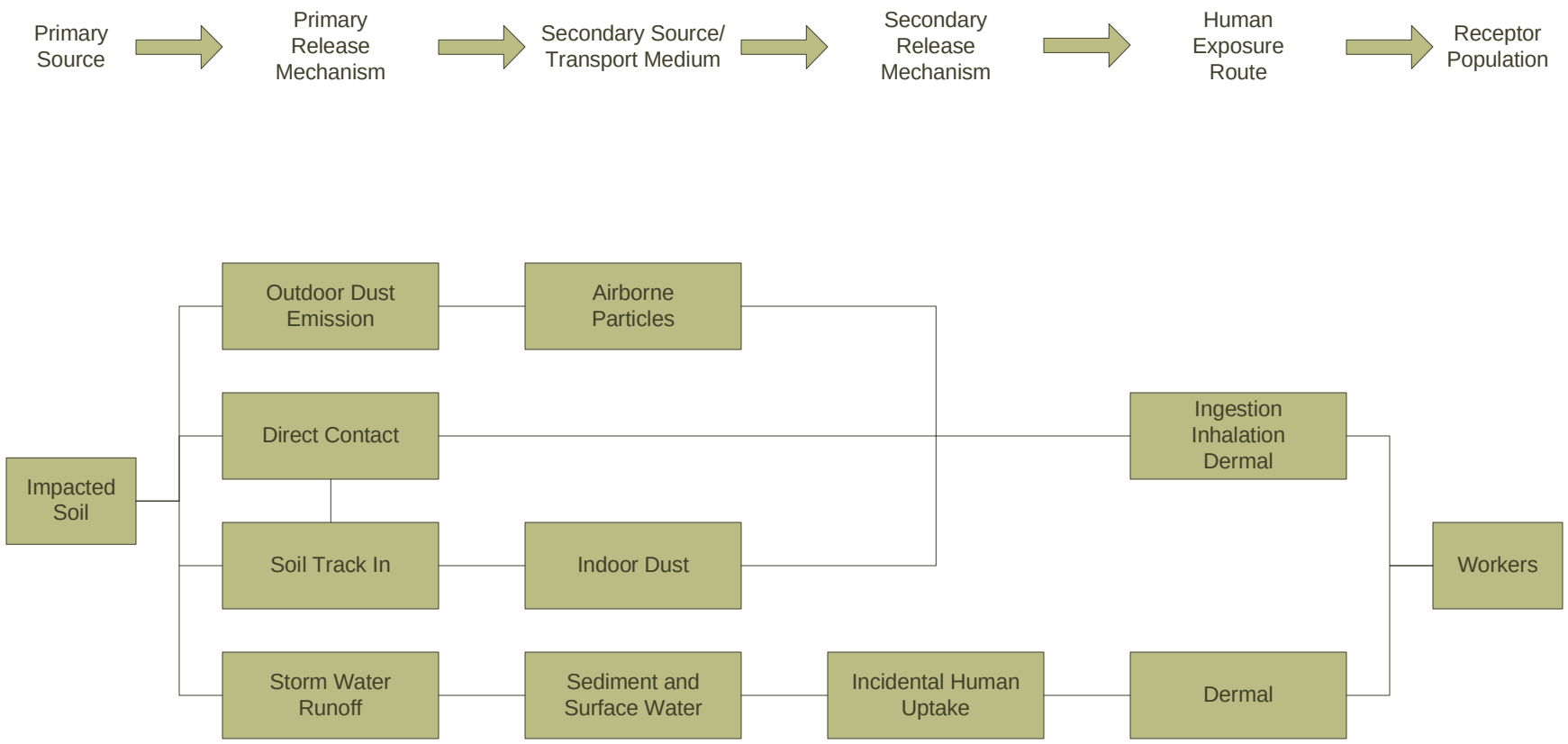

Figure 2. Midland Area Soils Conceptual Human Exposure Model for Industrial and Commercial Land Use

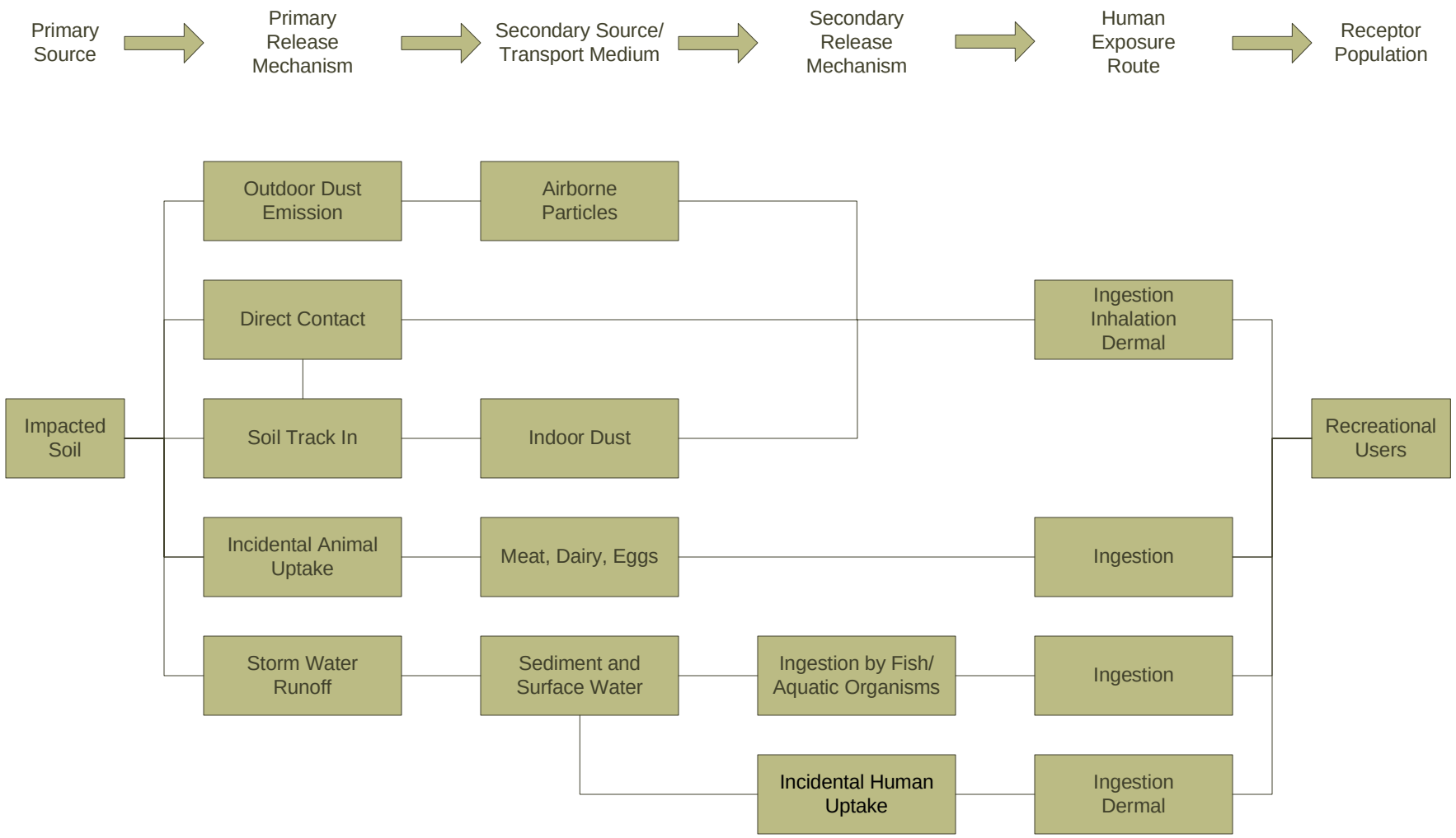

Figure 3. Midland Area Soils Conceptual Human Exposure Model for Recreational Land Use

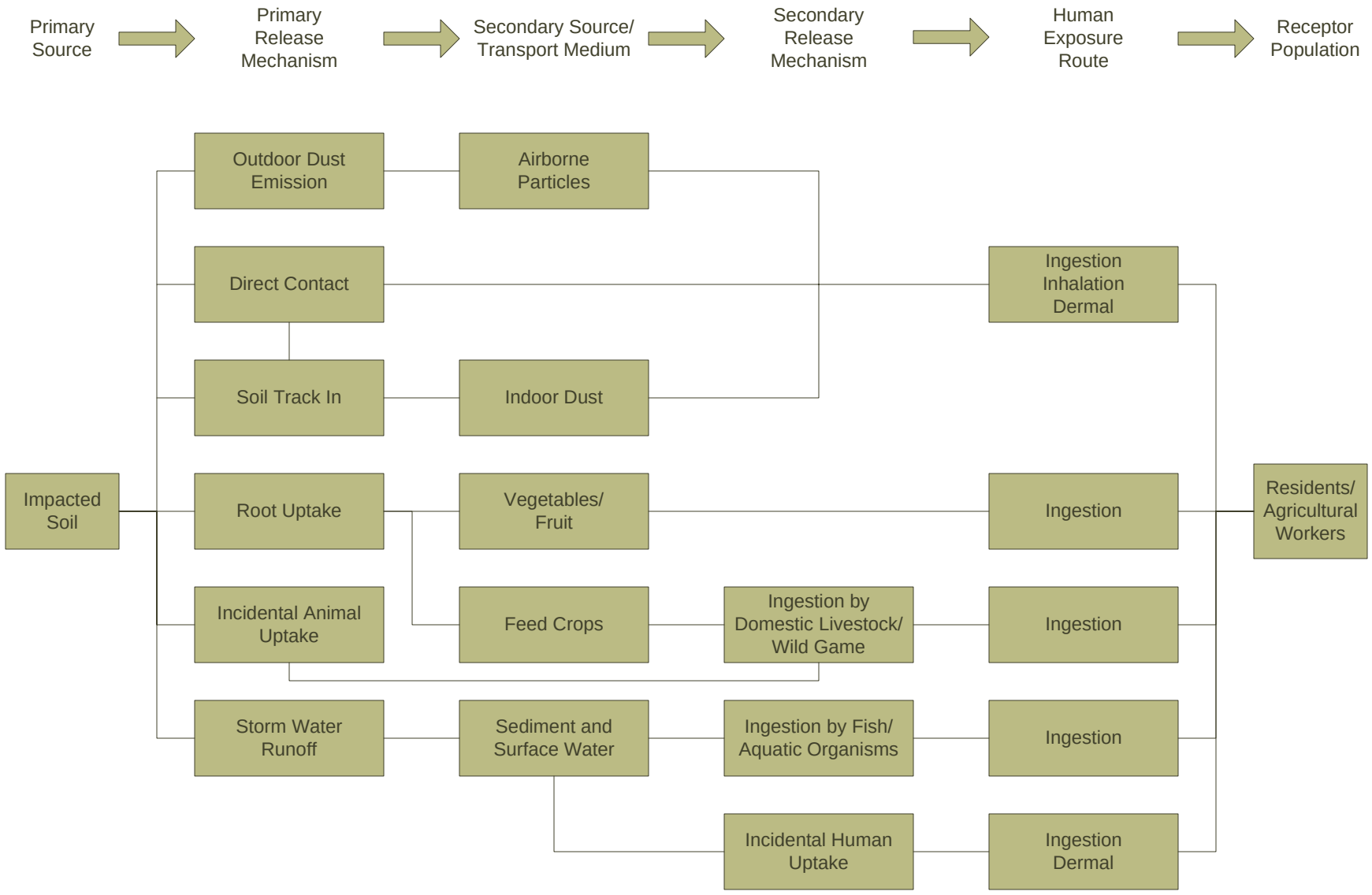

Figure 4. Tittabawassee River Floodplain Conceptual Human Exposure Model for Residential and Agricultural Land Uses

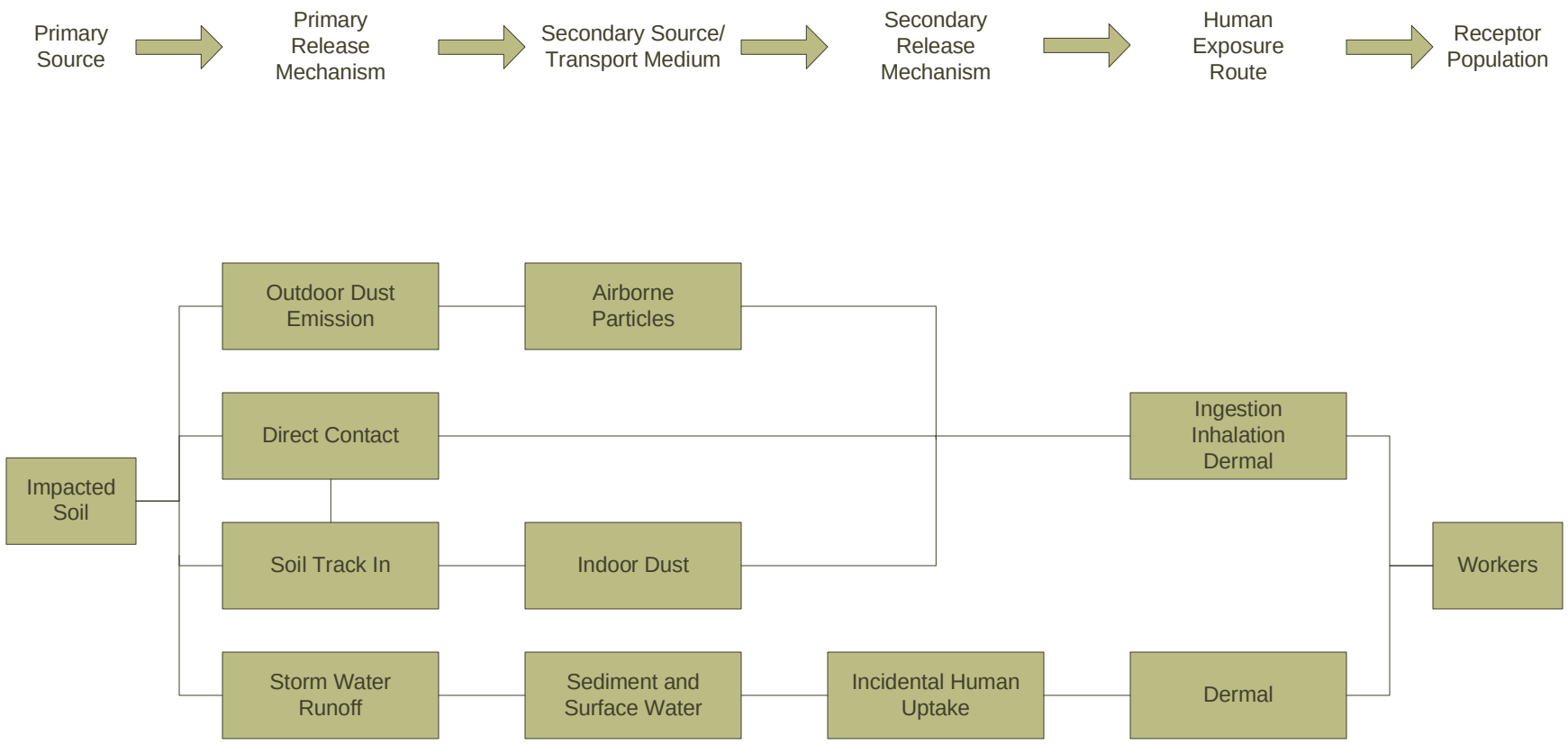

Figure 5. Tittabawassee River Floodplain Conceptual Human Exposure Model for Industrial and Commercial Land Uses

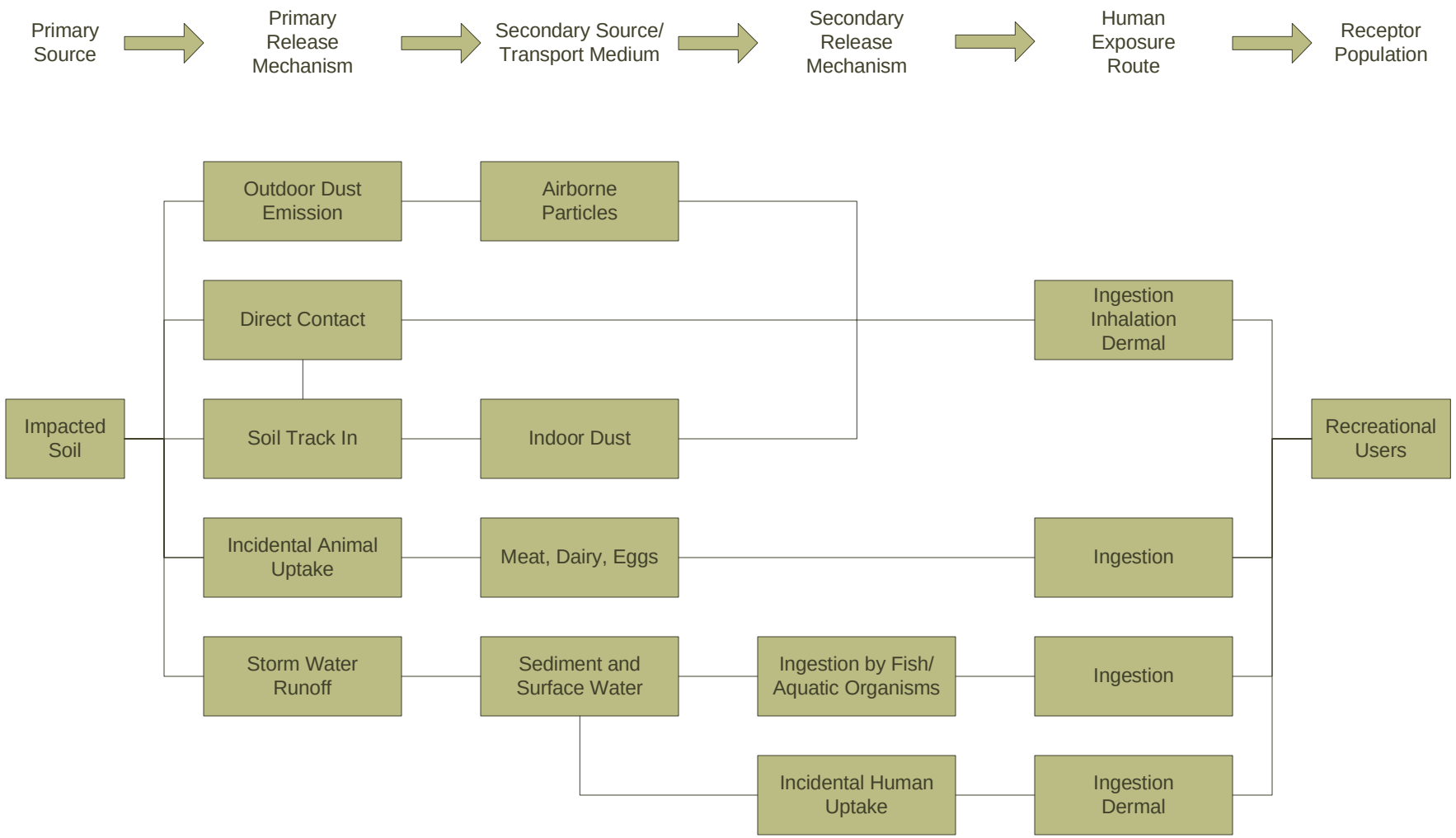

Figure 6. Tittabawassee River Floodplain Conceptual Human Exposure Model for Recreational Land Use